Appendices on the article "Reactive precipitation of vaterite calcium carbonate microspheres in supercritical carbon dioxide-water dispersion by microfluidics"



1. Experimental setup

Figure A1. Assembly of heating cartridge system for sapphire capillary

Figure A1 shows the different parts of the waterblock device presented in section 2.3 in the article. The water circulation chamber (or heating cartridge system with water inlet/outlet) was designed using a CAD drawer and prototyped (Fig. A1-a) with the OBJET30 3D inkjet printer (Stratasys. Eden Prairie. USA). The 3D printing material used for both parts was the VeroWhitePlus RGD835 (Stratasys. Eden Prairie. USA) which was processed at a temperature below 48°C. It was covered with an aluminum heat-conducting plate (Fig. A1-b) to optimize heat transfers between the circulating water and the sapphire capillary (Fig. A1-c). The latter is used for visualizations with a microscope which is surmounted with a fast camera.

2. Reproducibility tests

Repeatability tests were conducted for the different conditions. Typically, Figures A2 and A3 represent the size distribution variability of the particles, for the same experimenter at respectively 6 and 1 mL/min of each phase. The particles formulated at 6 mL/min show a good repeatability with always a similar size distribution: monodisperse with a low mean diameter and moderate variation of the mean diameter for the different runs (Figure A2). For a flow rate of 1 mL/min (Figure A3), the size distribution is consistent with a polydisperse distribution which does not vary significantly for three independent runs.



Figure A2. Repeatability tests of the CaCO₃ particles formulation (n=3). Conditions: 40°C, same flow rate for the scCO₂ and the aqueous calcium chloride solution: 6 mL/min, static micromixer, P = 250 bar, without polymer. Particle diameter distribution determined from several SEM images: n=1---. n=2 --- or n=3 ---



Figure A3. Repeatability tests of the CaCO₃ particles formulation (n=3). Conditions: 40°C, same flow rate for the scCO₂ and the aqueous calcium chloride solution: 1 mL/min, static micromixer, P = 250 bar, without polymer. Particle diameter distribution determined from several SEM images: n=1---. n=2 --- or n=3 ---

Results obtained by two different experimenters were also compared. The particle's mean diameters and standard deviations presented in Table A1 follow the same tendency for both experimenters. The measured diameters are similar and within standard deviation range. It can be concluded that the formulation and the SEM image analysis are reproducible. Moreover, whatever the experimenter, we can observe that variations of size distributions within the 6 mL/min formulations are negligible compared to the variations for formulations obtained at 1 or 3 mL/min. It confirms that the size distributions obtained for each flow rate are significantly different.

Table A1. Impact of the experimenter on the particle's synthesis and the SEM images analysis. Experimenter a): n = 2 / Experimenter b): n = 3. Conditions: 40°C, same flow rate for the scCO₂ and the aqueous calcium chloride solution as indicated, static micromixer, P = 250 bar.

Flow rate of each phase (mL/min)	1	3	6
Diameter (µm) - Experimenter 1	$3.0\pm0.8~\mu m$	$2.9\pm0.8~\mu m$	$1.6\pm0.3~\mu m$
Diameter (µm) - Experimenter 2	$2.5\pm1.6\mu m$	$2.9\pm1.0\mu m$	$1.8\pm0.3~\mu m$

Finally, Figure A4 shows that the variation of particle size's distribution between two experimenters is lower than the difference observed for an experiment conducted with or without PE6400. This confirms that the presence of polymer decreases the diameter of the CaCO₃ particles within experimental error.



Figure A4. Impact of the presence of polymer on the microfluidic process. Conditions: 40°C, same flow rate for the scCO₂ and the aqueous calcium chloride solution (6 mL/min), static micromixer, P = 250 bar. Particle diameter distribution determined from several SEM images: Without polymer: —, or with PEO₁₃-PPO₃₀-PEO₁₃—. a) Experimenter 1, b) Experimenter 2.

3. Effect of the different parameters

3.1. Effect of pressure



Figure A5. Impact of the pressure on the microfluidic process. Conditions: 40°C, same flow rate for the scCO₂ and the aqueous calcium chloride solution at 3 mL/min, static micromixer, different pressures, without polymer. a) Representative scanning electron microscopy (SEM) images of the CaCO₃ particles. From left to right (yellow. Green. Red): 150. 200 and 250 bar, b) particle diameter distribution determined from several SEM images: 150 bar –. 200 bar – and 250 bar –

3.2. Effect of the flow rates ratio of the scCO₂ and aqueous phases



Figure A6. Impact of the flow rate ratio of each phase at constant total flow rate (12 mL/min) on the microfluidic process. Conditions: 40°C, different flow rates for the scCO₂ and the aqueous calcium chloride solution, respectively (in mL/min), coflow micromixer, P = 250 bar. a) Representative scanning electron microscopy (SEM) images of the CaCO₃ particles (green, red and blue): 8/4, 6/6 and 4/8 mL/min, b) particle diameter distribution determined from several SEM images: 8/4 - .6/6 - ... and 4/8 - ...



Figure A7. Impact of the total flow rate on the microfluidic process. Conditions: 40° C, same flow rate for the scCO₂ and the aqueous calcium chloride solution, static micromixer, P = 250 bar, without polymer. a) Representative scanning electron microscopy (SEM) images of the CaCO₃ particles. from left to right (yellow. blue. red): 1, 3 and 6 mL/min for each phase, b) particle diameter distribution determined from several SEM images: 1---. 3 --- and 6 --- mL/min for each phase.

3.3. Addition of polymer

3.3.1. Characterization of the amphiphilic character of PEO13-PPO30-PEO13

The interfacial tension measurements were performed on a high pressure / high temperature experimental bench developed in partnership with Top Industrie and controlled by the Windrop® software (Teclis). The bench was composed of a motorized and variable volume view cell (Top Industrie) for the scCO₂ injection and a syringe pump (260D P2 ISCO. USA)

for the injection of the aqueous solution containing the amphiphilic copolymer. This solution was injected in a 50 mL magnetically stirred measurement cell (Top Industrie) equipped with a light source. A video camera was mounted on an optical rail for proper alignment and connected to a computer for video acquisitions. The measurement cell initially contained a small amount of water (approx. 3 mL) stirred to ensure the CO₂ phase saturation. The CO₂ was first injected to the desired pressure and the cell was thermalized at 40°C with a heated bath (Fisherbrand Isotemp 6200H7). Then, the aqueous polymer solution was introduced in the measurement cell with the syringe pump to obtain a 5 μ L pendant drop by setting a desired pressure (typically 3 to 5 bar above the pressure of the measurement cell to avoid backflow). Finally, the interfacial tension measurement between the aqueous solution and the water-saturated CO₂ was started and maintained, keeping the volume of the droplet constant until γ remained stable for at least 2 minutes.

Figure A8 reveals a strong decrease of γ in the presence of PEO₁₃-PPO₃₀-PEO₁₃ compared to the same conditions without polymer.



Figure A8. Average interfacial tension as a function of the pressure with 1% wt% PEO₁₃-PPO₃₀-PEO₁₃ \bigcirc and without polymer \square . The three measurements performed for each condition are represented on the figure to give an idea of the reproducibility.

Emulsions of water and scCO₂ were prepared in the variable volume view cell. First, the studied copolymer was solubilized in deionized water and placed in the view cell. Then. scCO₂ was injected to the desired volume fraction and the pressure was controlled with the syringe pump. The temperature of the apparatus was controlled with the heated bath. The copolymer/water/ scCO₂ mixture was emulsified at 900 rpm with a spiral propeller blade for 15 min.



Figure A9. Typical pictures of the water/scCO₂/PEO₁₃-PPO₃₀-PEO₁₃ mixtures in different states at 250 bar and 40°C: (a) before emulsification, (b) just after emulsification during 15 minutes at 900 rpm.

Figure A9 shows that PEO_{13} -PPO₃₀-PEO₁₃ stabilizes the water/scCO₂ emulsion. Phase separation typically does not occur before 60 min.

3.3.2. Results of the CaCO₃ precipitation experiments in the presence of polymer



Figure A10. Impact of the flow rate of each phase on the microfluidic process – in the presence of a polymer and with a coflow micromixer. Conditions: 40° C, same flow rate for the scCO₂ and the aqueous calcium chloride solution, coflow micromixer, P = 250 bar, in the presence of polymer: *PEO*₁₃-*PPO*₃₀-*PEO*₁₃ at 1 wt%. a) Optical images of the dispersion within the microfluidic channel. from left to right (yellow. blue. red): 1. 3 and 6 mL/min for each phase, b) representative scanning electron microscopy (SEM) images of the CaCO₃ particles (same color code and order), c) particle diameter distribution determined from several SEM images: 1---. 3 --- and 6 --- mL/min for each phase.



Figure A11. Impact of the flow rate of each phase on the microfluidic process in the presence of a polymer and with a static micromixer. Conditions: 40°C, same flow rate for the scCO₂ and the aqueous calcium chloride solution, static micromixer, P = 250 bar, in the presence of polymer: *PEO*₁₃-*PPO*₃₀-*PEO*₁₃ at 1 wt%. a) Optical images of the dispersion within the microfluidic channel. from left to right (yellow. blue. red): 1. 3 and 6 mL/min for each phase. At 3 and 6 mL/min, the droplets of dispersed phase are so small that they cannot be distinguished by the camera leading to an opaque dispersion, b) representative scanning electron microscopy (SEM) images of the CaCO₃ particles (same color code and order), c) particle diameter distribution determined from several SEM images: 1 - . 3 - and 6 - mL/min for each phase.



Figure A12. Impact of the type of micromixer in the presence of polymer. Conditions: 40° C, same flow rate for the scCO₂ and the aqueous calcium chloride solution, different micromixers, P = 250 bar, with 1 wt% of PEO₁₃-PPO₃₀-PEO₁₃ in the aqueous phase. a) Optical images of the dispersion within the microfluidic channel at flow rates of 1……. 3 --- and 6 - mL/min of each phase with the coflow (blue) or static (red) micromixer, b) scanning electron microscopy images of the CaCO₃ particles obtained at a flow rate of 3 mL/min of each phase with the coflow (blue) or static (red) micromixer distribution of the CaCO₃ particles obtained at a flow rate of 3 mL/min of each phase with the coflow (blue).

Figure A12 shows that in the presence of 1 wt% of PEO_{13} - PPO_{30} - PEO_{13} in the aqueous phase, the dispersion is improved with a static micromixer compared to a co-flow one, particularly at a flow rate of 3 and 6 mL/min. However, at a flow rate of 3 mL/min, changing the type of micromixer and keeping the other parameters constants changes the most the dispersion state, but only weakly affects the diameter of the CaCO₃ particles. Actually, the CaCO₃ particles seem slightly smaller with the co-flow micromixer than with the static one, although the dispersion is better with the latter than with the former micromixer. In other words, improving the dispersion state of the phases using the static micromixer in the presence of polymer does not decrease the diameter of the CaCO₃ particles.

Table A2. Results of the study of the influence of polymer on the characteristics of the CaCO₃ particles – Different pressures and flow rates of the phases. Conditions: 40° C, different flow rates, Coflow micromixer, different pressures between 100 and 250 bar, without or with polymer (1 wt% in the aqueous phase). ND = Not Determined.

Pressure	Rate of flow scCO2/Water (mL/min)	Polymers	Diameter (µm)	Yield (%)
	1/2	Without polymer	2.6 ± 0.4	ND
		PDMS ₁₃ - <i>b</i> -POEGMA ₄₆	1.5 ± 0.4	61
		PEO ₁₃ -PPO ₃₀ -PEO ₁₃	1.3 ± 0.4	67
		Dextran (40 000 g.mol ⁻¹)	2.0 ± 0.7	ND
		POEGMA	2.2 ± 0.6	56
_	2/1	Without polymer	2.9 ± 0.7	ND
		PDMS ₁₃ - <i>b</i> -POEGMA ₄₆	1.3 ± 0.3	53
		PEO ₁₃ -PPO ₃₀ -PEO ₁₃	1.4 ± 0.3	57
		Dextran (40 000 g.mol ⁻¹)	1.8 ± 0.6	ND
150 har		POEGMA	1.3 ± 0.2	49
130 bar –		Without polymer	2.4 ± 0.5	ND
	4/8	PDMS ₁₃ - <i>b</i> -POEGMA ₄₆	1.6 ± 0.3	61
		PEO ₁₃ -PPO ₃₀ -PEO ₁₃	1.2 ± 0.4	67
		Dextran (40 000 g.mol ⁻¹)	1.9 ± 0.3	ND
		POEGMA	1.9 ± 0.6	56
	8/4	Wihtout polymer	$\textbf{2.8} \pm \textbf{0.6}$	ND
		PDMS ₁₃ - <i>b</i> -POEGMA ₄₆	1.1 ± 0.3	53
		PEO ₁₃ -PPO ₃₀ -PEO ₁₃	1.6 ± 0.4	49
		Dextran (40 000 g.mol ⁻¹)	1.6 ± 0.3	ND
		POEGMA	1.7 ± 0.3	56
	1/2	Without polymer	2.5 ± 0.6	ND
		PDMS ₁₃ - <i>b</i> -POEGMA ₄₆	1.3 ± 0.3	ND
		PEO ₁₃ -PPO ₃₀ -PEO ₁₃	1.8 ± 0.6	ND
		Dextran (40 000 g.mol ⁻¹)	1.6 ± 0.7	ND
	2/1	Without polymer	$\textbf{2.5} \pm \textbf{0.8}$	ND
		PDMS ₁₃ -b-POEGMA ₄₆	1.5 ± 0.3	ND
		PEO ₁₃ -PPO ₃₀ -PEO ₁₃	1.2 ± 0.7	61
		Dextran (40 000 g.mol ⁻¹)	1.3 ± 0.3	45
250 001	4/8	Without polymer	2.5 ± 0.5	64
_		PDMS ₁₃ - <i>b</i> -POEGMA ₄₆	1.2 ± 0.2	ND
		PEO ₁₃ -PPO ₃₀ -PEO ₁₃	1.2 ± 0.4	77
		Dextran (40 000 g.mol ⁻¹)	1.5 ± 0.4	ND
	8/4	Without polymer	2.6 ± 0.3	53
		$PDMS_{13}$ - b - $POEGMA_{46}$	1.1 ± 0.2	ND
		PEO ₁₃ -PPO ₃₀ -PEO ₁₃	1.1 ± 0.3	47
		Dextran (40 000 g.mol ⁻¹)	1.8 ± 0.6	ND

Table A3. Results of the study of the influence of polymer on the characteristics of the CaCO₃ particles – Different pressures and PDMS₁₃-*b*-POEGMA_x with different DP_n (x) of the POEGMA block. Conditions: 40°C, Flowrates: 3 mL/min scCO₂ / 3 mL/min aqueous solution of calcium chloride, Coflow micromixer, without or with polymer (1 wt% in the aqueous phase). ND = Not Determined.

Rate of flow scCO2/Water (mL/min)	Pressure	Polymers	Diameter (µm)	yield(%)
3/3	100 bar	Without polymer	4.0 ± 1.0	59%
		PDMS ₁₃ - <i>b</i> -POEGMA ₁₆	2.6 ± 0.4	ND
		PDMS ₁₃ - <i>b</i> -POEGMA ₃₁	3.2 ± 0.5	ND
	150 bar	Without polymer	3.7 ± 0.1	ND
		PDMS ₁₃ - <i>b</i> -POEGMA ₁₆	2.2 ± 0.3	ND
		PDMS ₁₃ - <i>b</i> -POEGMA ₃₁	2.5 ± 0.5	ND
		Without polymer	3.7 ± 0.7	ND
	200 bar	PDMS ₁₃ - <i>b</i> -POEGMA ₁₆	1.6 ± 0.4	63
		PDMS ₁₃ - <i>b</i> -POEGMA ₃₁	2.1 ± 0.5	57
	250 bar	Without polymer	3.7 ± 0.7	61
		PDMS ₁₃ - <i>b</i> -POEGMA ₁₆	2.0 ± 0.6	64
		PDMS ₁₃ - <i>b</i> -POEGMA ₃₁	1.8 ± 0.5	ND

3.4. Surface mapping of PDMS13-b-POEGMA46 on the CaCO3 particles by EDX-MEB



Figure A13. Impact of presence of polymer. Conditions: 40° C, $4 \text{ mL/min of scCO}_2$ and 8 mL/min of aqueous calcium chloride solution, P = 250 bar, with 1 wt% PDMS₁₃-b-POEGMA₄₆. a) Scanning electron microscopy images of the CaCO₃ particles. X-ray elemental mapping : b) Calcium and c) silicon