

Supporting information

XPS spectra of dry microcapsules were recorded using a Kratos AXIS Ultra DLD spectrometer with a monochromated Al K α radiation source ($h\nu = 1486.7$ eV) operating at 15 kV and 10 mA. The pressure in the vacuum chamber during the analysis was less than 10^{-10} bar, and the take-off angle of the photoelectrons was perpendicular to the sample. The areas under selected photoelectron peaks in the spectrum were used to calculate the percentage atomic concentrations. High-resolution (0.1 eV) spectra were then recorded for pertinent photoelectron peaks at a pass energy of 20 eV to identify the chemical state of each element. All the binding energies (BEs) were referenced to the C1s neutral carbon peak at 285 eV, to compensate for the effect of surface charging. The processing and curve-fitting of the high resolution spectra was performed using CasaXPSTM software. The analysis area was 700×300 μm .

The surface chemistry of the dry microcapsules (and silica nanoparticles for comparison) was analysed by X-ray photoelectron spectroscopy (XPS) (Table 1). It can be seen (Table 1) that the microcapsule surfaces are composed of both silica and carbon from the oil phase and emulsifiers; thus, the microcapsule surface has a dual hydrophilic-lipophilic character that can explain redispersibility in aqueous environment. Surface chemistries are significantly different for microcapsules formed at the beginning of region II (Scheme 1) with 10 wt% silica relative to droplets, in comparison with those prepared with higher levels of silica. That is, the surface carbon atomic concentration (based on C1s) increases from ~47 % to ~60 % and the silicon atomic concentrations (based on Si 2p) increases from ~7 to ~14 % as the level of silica inclusion increases. Close spectral inspection of the C1s region showed peaks from the triglycerides at the microcapsule surfaces, i.e. at 286.62 eV generated by the

carbon adjacent to hydroxyl ($-C-O-H$), 289 eV due to the ester carbon and the signal at 285.62 eV corresponding to C-N. The small C1s signals (3 to 4 %) in pure silica samples can be attributed to adventitious carbon impurities, unavoidable during measurements. High resolution Si2p peak analysis showed that both SiO₂ matrix and silicate peaks at 101.63 eV were present in microcapsules OA 10 and 15 % (Fig. 1) whereas microcapsules with > 15 wt% silica showed a single Si2p peak at 102.92 eV (Fig. 1) corresponding to the SiO₂ matrix. Equivalent microcapsules prepared by spray drying with 5wt% silica showed both SiO₂ and silicate peaks at 101.63 eV²¹. The presence of small nitrogen and silicate peaks for microcapsules from the beginning of region II are considered as a consequence of the charge neutralisation between silica and the amino groups from oleylamine at lower silica levels (Fig. 1). For microcapsules with > 15 wt% silica the N 1s peak disappears due to obscuration by silica nanoparticles.

Table 1. XPS spectral and TGA analysis of phase coacervated microcapsules

Sample ^[a]	Si 2p (%) 101.79 eV	C 1s (%) 283.39 eV	O 1s (%) 532.69 eV	N1s (%) 398.59 eV	Oil content (wt %) ^[b]	Oil entrapment efficiency (wt %)
OA10%	9.198	60	30.531	0.271	72.58	80
OA15%	12.343	52.1	35.416	0.141	60.79	81.51
OA20%	13.920	48.7	37.38	0	60.61	85.76
OA25%	13.553	47.5	61.053	0	60.65	80.86
OA30%	13.6	46.8	39.600	0	64.43	85.9
S	27.33	3.67	69.000	0	0	0

[a] OA-oleylamine based; S-pure silica powder; numbers on right-hand side- wt% silica relative to droplets in the aqueous phase [b] determined by TGA

