Supplementary Material for

Eco-friendly silica microcapsules with improved fragrance retention

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1. Synthesis and Characterization of Silica Microcapsules with Silica Derivatives

Silica derivatives (MTMS, DMDES, N-OTES, and APTES) was mixed with TEOS in a molar ratio of 0.5 : 99.5 and the TEOS mixture was mixed with hexyl cinnamaldehyde in a weight ratio of 1:1 in the oil phase. CTAB (10 wt%) was dissolved in DI water at 80 °C. After complete dissolution, the concentrated CTAB solution was diluted to 1.5 mM with DI water. The oil phase was gradually added to the aqueous phase and mixed using a homogenizer at 3,000 rpm (T-25 Ultra-Turrax, IKA). The mixture was subsequently homogenized at 11,000 rpm for 10 min to form the fragrance O/W emulsion. The emulsion was maintained at 25 °C for two days, during which time microcapsules with premature silica shells formed. The thickness of the silica microcapsules were enhanced by adding varying amounts of TEOS (1, 3, 5 wt%) to the precapsule dispersion and mixing for 10 min with a mechanical overhead stirrer (Eurostar 20, IKA) at 200 rpm. The reaction was allowed to proceed at 25 °C for three days, after which the silica microcapsules were centrifuged and rinsed with DI water. The resulting pellets were dried in an oven at 40 °C for 48 h.

The fragrance compound in the silica microcapsules was completely removed prior to analysis of the various silica microcapsules. The dispersion process in ethanol, thorough crushing with a tip sonicator (Qsonica, CT), and precipitation by centrifugation was repeated six times. After centrifugation, the silica shell particles were freeze-dried for 24 h and then dried at 100 °C for one week to obtain a pure silica shell. FT-IR spectra of the silica shells were obtained using an FT-IR spectrometer (Spectrum TWO LiTa, Perkin Elmer).

Core–shell silica microcapsules have been synthesized by a silica reaction in which hydrolyzed TEOS is associated with the emulsion surface. Cationic emulsifiers and silica derivatives (MTES, DMDS, N-OTES) can be used to modify the properties of silica microcapsules to enhance silica deposition or capsule performance [1, 2].

To confirm the feasibility of using the modified microcapsules, we first synthesized microcapsules using an emulsion template. The corresponding silica shells, obtained after completely removing the fragrance compound from the microcapsules, were then analyzed by FT-IR spectroscopy. As shown in Figure S1, after adding silica derivatives containing alkyl groups, the FT-IR spectrum of the silica shells revealed a C–H vibration at 2978 cm^{-1} corresponding to a methyl group. This methyl peak did not appear when only TEOS was used. According to the ECHA report on intentionally added microplastics [3], silica particles are considered to be microplastics if their surfaces are modified with alkyl groups or hydrophobically modified derivatives. We therefore sought to develop microcapsules using only silica.

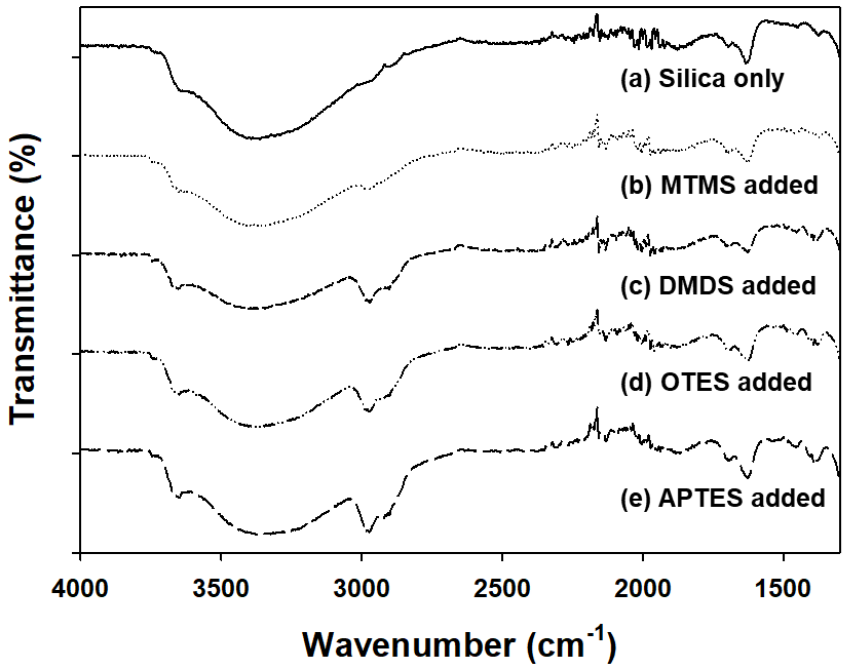
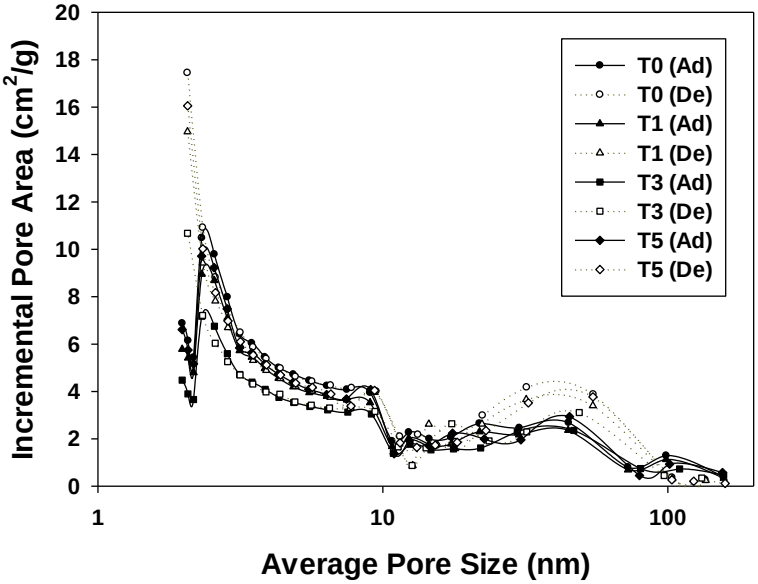


Figure S1. Fourier-transform infrared spectra of silica microcapsules synthesized using (A) TEOS, TEOS with added (B) MTMS, (C) DMDS, (D) N-OTES, and (E) APTES.

(A)



(B)

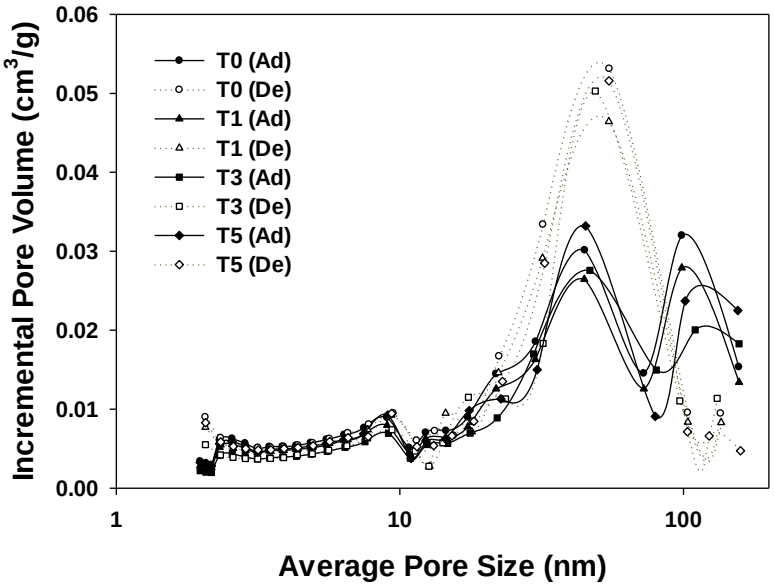


Figure S2. (A) Incremental pore areas and (B) incremental pore volumes as functions of average fragrance microcapsule pore size according to additional TEOS treatment.

Table S1. Fragrance remaining within T5 microcapsules in 15% SDS solution at 60 ℃ after 12 days according to the speed and duration of overhead stirring, and additional TEOS was emulsified.

Speed (RPM)	Time (min)	Remaining Fragrance after 12 days (%)
100	10	65.06 ± 4.1531
200	5	68.19 ± 3.8461
200	10	75.29 ± 2.5974
200	30	75.67 ± 1.7154
400	10	75.53 ± 2.0842
800	10	75.76 ± 1.1054

References

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3. Annex XV restriction report proposal for a restricton substance; European Chemicals Agency (ECHA): Helsinki, Finland, 2019.