

Supporting Information “Mechano-responsive microcapsules with thin, homogeneous shells”

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Quantification of shell thickness

The shell thickness of the double emulsion drops cannot be directly quantified from optical microscopy images because it is at or below the resolution limit. To overcome this limitation, we indirectly quantify the shell thickness, as has previously been described.¹⁻⁵ Briefly, we quantify the outer radius of the double emulsion drop, R_0 , using optical microscopy. The drop is subsequently ruptured by adding isopropanol to the outer phase and the radius of the resulting oil drop, r , is measured using again optical microscopy.¹ Through volume conservation we obtain:

$$\frac{4}{3}\pi R_0^3 - \frac{4}{3}\pi(R_0 - t_s)^3 = \frac{4}{3}\pi r^3$$

such that the shell thickness, t_s , is determined as:

$$t_s = R_0 - (R_0^3 - r^3)^{\frac{1}{3}}.$$

To check the accuracy of this method, we quantify the shell thickness of double emulsions with thick shells using optical microscopy and compare these values to those obtained from volume conservation calculations. In addition, we compared these results to values obtained from optical microscopy images of compressed double emulsions.⁵ The values obtained from all three different measurement methods are in good agreement, suggesting that the use of isopropanol to rupture drops does not introduce systematic measurement errors.¹

Quantification of capsule footprint

The footprint of capsules is defined as the volume fraction of the double emulsion or capsule occupied by the shell. Because perfluorinated polymers have a low affinity to water, we assume the perfluorinated polymers to be collapsed if dispersed in aqueous solutions such that we approximate the shell thickness of capsules, d , in aqueous solutions to be similar to that measured in the dry state. Using this approximation, we estimate the volume fraction of the capsule occupied by the shell, the footprint F , as

$$F = \frac{(R_0^3 - (R_0 - d)^3)}{R_0^3}$$

Load applied on capsules.

To qualitatively assess the rupture strength of capsules, 20 μL of capsules are deposited on a glass slide. Those capsules are compressed by a $1 \times 1 \text{ cm}^2$ glass slide that is loaded with different weights. Optical images are taken after samples have been compressed with different weights and are used to determine the fraction of intact capsules, as shown in Figure S1.

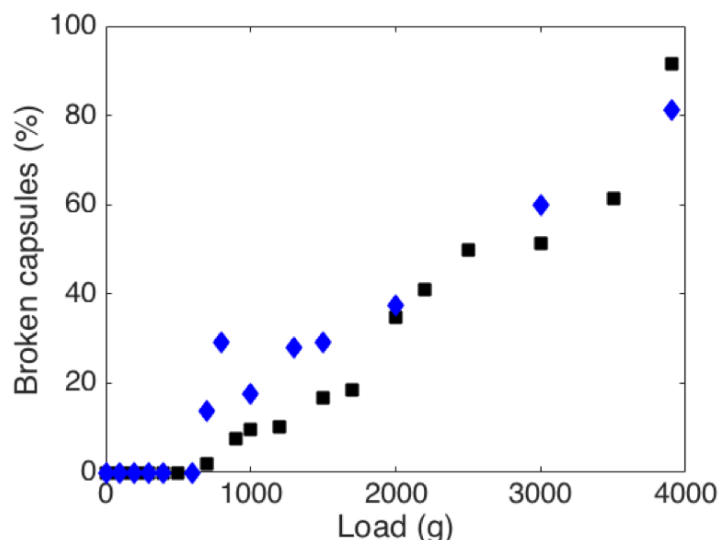


Figure S1: (A) Percentage of broken capsules whose shell is (■) thin and homogeneous and (◆) thick and heterogeneous as a function of the load applied on the top glass slide.

Quantification of the applied pressure

To convert the osmotic pressure difference into the pressure acting on the capsule shell, we use the Van't Hoff law: $\pi = 2\Delta cRT$; here π is the pressure applied to the capsule, Δc is the difference of osmolarity between the core and the outer phase of the capsule, R the gas constant, and T the temperature of the surrounding.

Quantification of the permeability of capsules

To measure the permeability of capsules, we disperse 60 μL of polymerized capsules with thin shells, whose core is labelled with 2% patent V, into an eppendorf tube containing 1 mL of deionized water. To acquire statistics, each data point is measured on four independent samples. The amount of dye contained in the supernatant is quantified as a function of the incubation time using UV-Vis spectroscopy, as exemplified in Figure S2.

The maximum intensity absorbance for the blue dye, A , is obtained at $\lambda = 637.5$ nm. This value is used to quantify the amount of blue dye contained in the supernatant.

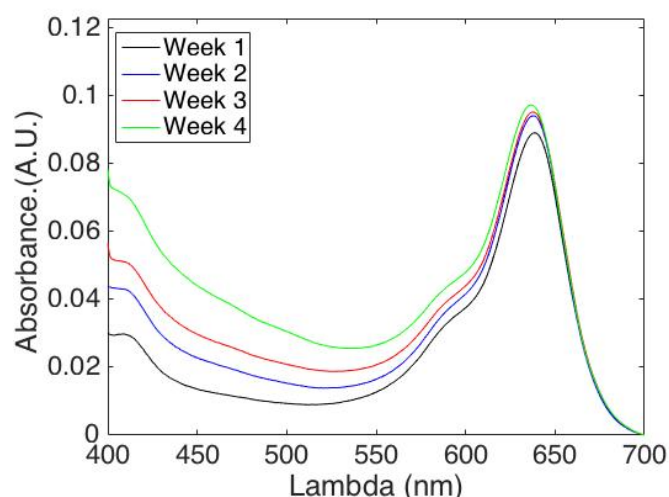


Figure S2: UV-VIS absorption spectra measured for capsules with thin shells as a function of time.

Calculation of cumulative leakage

To estimate the maximum amount of dye that can leak from double emulsions, we disperse 0.06 mL of an aqueous solution containing 2% blue dye in 1 mL of deionized water; this volume corresponds to the estimated cumulative

volume of all the capsule cores contained in a sample. We quantify the intensity of this solution using UV-VIS spectroscopy and use this value to normalize all our results:

$$I = \frac{A}{A_{max}}$$

Permeability of capsules towards fluorescein

If fluorescein is incorporated into the core of double emulsions, it bleaches while they are exposed to UV light required to initiate the polymerization reaction of the monomers. Therefore we cannot incorporate fluorescein in the core of the capsules. Instead, we produce empty double emulsions, convert them into capsules with thin shells, and incubate them in an aqueous solution containing 0.1wt% fluorescein. After four days, the capsules are washed thoroughly to remove traces of fluorescein in the outer medium. Fluorescence microscopy images do not reveal any fluorescence in the core of these capsules, as exemplified in the fluorescent image in Figure S3. These results demonstrate that no significant amounts of fluorescein diffuse into the capsule, indicating that these capsules are for practical purposes impermeable even towards low molecular weight encapsulants.

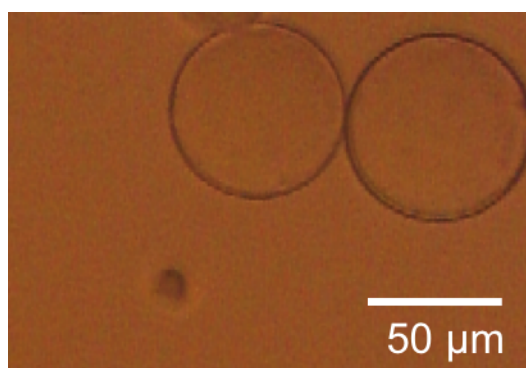


Figure S3: Overlay optical and fluorescence micrographs of capsules incubated in a fluorescein-containing aqueous solution for 4 days after they have been washed.

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