Supplementary information

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The following is the supporting information related to the paper entitled *"Relaxation dynamics in single polymer microcapsules probed with laser-generated GHz acoustic waves"*.

1 Microcapsule preparation

PLGA was dissolved into 4 mL of methylene chloride along with the desired amount of liquid PFOB and placed in a thermostated bath maintained at 20 C to ensure full miscibility of the PFOB. The organic solution was then emulsified into 20 mL of 1.5% sodium cholate (w/v) aqueous solution using an Ultraturrax T25 (IKA) operating with a SN25-10G dispersing tool at a velocity of 8000 rpm. Emulsification was performed in a 50 mL beaker placed over ice for 2 min. Methylene chloride was then evaporated by magnetic stirring for about 3 h at 300 rpm in a thermostated bath (20 C). For fluorescent or confocal microscopy, Nile Red was added to the organic solution prior to emulsification. Typically, about 100 μL of a concentrated Nile Red solution (0.057 mg/mL in methylene chloride) was added to the organic solution prior to emulsification.[1]

2 Thickness determination

Samples in water were placed between glass slides and examined with a Zeiss LSM-510 confocal scanning laser microscope equipped with a 1 mW helium neon laser, using a Plan Apochromat 63X objective (NA 1.40, oil immersion). Red fluorescence was observed with a long-pass 560 nm emission filter under 543 nm laser illumination. The pinhole diameter was set at 71 μ m. Stacks of images were collected every 0.42 μm along the z axis. Particle size and shell thickness were measured directly on the confocal images using either the Zeiss software or ImageJ (Scion Corporation). Measurements were carried out in the equatorial plane of each capsule to minimize the error due to the position of the slice. The size of a pixel was 70 nm. For the sodium cholate concentration and the rotation speed of the dispersing tool we used, the span of the distribution of microcapsule size is 0.57, as determined by laser diffraction granulometry.[1]

For each PLGA concentration, the ratio of the capsule radius to the shell thickness T/R is constant. The ratio T/R is estimated from confocal images for several PLGA concentrations, revealing a linear dependence of T/R vs concentration. Therefore, in the present opto-acoustic experiment, knowing the radius of the capsule (estimated optically) and the concentration of PLGA used ($T/R = 0.25 \pm 0.025$), the expected thickness is obtained. The thickness measured by the opto-acoustic technique is in good agreement with that expected.

3 Beam description

The laser beams are focused using a Nikon EpiPlan Fluor 50X objective (NA 0.8). The $1/e^2$ radius of the pump and probe spot sizes are measured from the Gaussian intensity profiles recorded by a CCD camera at ~ 2 and $1 \sim \mu$m at the focal point on a bare Ti6Al4V sample, respectively.[2]

The laser beam propagates at normal incidence in the direction $\vec{x}$. The absorbed electromagnetic energy is expressed from the Poynting vector[3] in the titanium substrate:

$$Q(x,r,t) = \gamma I_0 (1 - R_{ct} R_{ac}) f(t) g(r) e^{-\gamma x} \qquad (1)$$

with I_0 the incident energy per unit length. Functions $f(t)$ and $g(r) = \exp(-2r^2/\chi^2)$ are the time and axial Gaussian distributions of intensity of the mode-locked laser pulses, with r and χ the radial coordinate and the beam radius at $1/e^2$. $\gamma^{-1} = \lambda/4\pi n_t''$ is the optical penetration depth in titanium, where λ and n_t'' are the laser wavelength and the imaginary part of the refractive index in titanium. Typical values of n_t'' yields $\gamma^{-1} \sim 15$ nm at the pump wavelength.[4] Similiar values are obtained at the probe wavelength. R_{ct} and R_{ac} are the coefficients of optical reflection in intensity at the titanium/capsule and air/capsule interfaces, respectively. Owing to index matching between the core and the shell, the reflection coefficient at the core/shell interface is neglected.

References

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