

Electronic Supplementary Information

Uniform hydrogel-filled elastomer microcapsules structured with mechanically resilient complex shell layers

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Experimental part

Materials: We use an aqueous mixture of 10 wt% hydrogel monomer of poly(ethylene glycol) diacrylate (PEGDA, M_n 6000 $\text{g}\cdot\text{mol}^{-1}$, Sigma Aldrich), 0.4 wt% photoinitiator (2-Hydroxy-2-methylpropiophenone, Sigma Aldrich), 0.005 wt% fluorescence isothiocyanate (FITC)-labelled dextran (M_w 70,000 $\text{g}\cdot\text{mol}^{-1}$, Sigma Aldrich). As a middle phase, we use a solvent mixture of 1.5 - 7.5 wt% PU precursor (Secure SE-8110, Fotopolymer), 0.1 wt% poly (glycerin)-*b*-poly(ϵ -caprolactone) (PG-*b*-PCL) diblock copolymers, 0.002 wt% (Sigma Aldrich), toluene (Daejung) and chloroform (Daejung). The molecular weights of PG and PCL are 2200 $\text{g}\cdot\text{mol}^{-1}$ and 3500 $\text{g}\cdot\text{mol}^{-1}$, respectively. Monodisperse 10 wt% amorphous silica particles (KE-P100, KE-P10 Nippon Shokubai) are dispersed in middle phase after hydrophobic treatment with trimethoxy(octadecyl)silane (Sigma Aldrich). The mixing ratio of toluene and chloroform is set to 1/1 by weight. We use an aqueous mixture of 10 wt% polyvinyl alcohol (PVA, M_w 13000-23000 $\text{g}\cdot\text{mol}^{-1}$, Sigma-Aldrich).

Fabrication of microcapillary-based microfluidic devices: To fabricate glass capillary-based microfluidic devices, first, round capillaries are tapered by heating and pulling a cylindrical glass capillary (outer diameter = 1.0mm, inner diameter = 0.58mm, World Precision Instruments, USA) with a pipette puller (Model P-97, Sutter Instruments, USA). The glass capillary breaks into two tapered capillaries. The end tip of the tapered glass capillaries is cut to the designated diameters using a microforge station (Micro Forge MF 830, Narishige, Japan). The smaller round capillary tube used in this study is treated with hexyltrimethoxysilane to make their surfaces hydrophobic. For this, 1 wt% of hexyltrimethoxysilane (TCI) in toluene is flowed through the capillary and dried at 50 °C for 6 h. The other collection round capillary tube is treated with 2-[methoxy (polyethyleneoxy)-propyl] trimethoxyl silane (Gelest)

to modify the surface hydrophilic. This selected treatment of the capillary surface prevents wetting of middle phase from the inner wall, thus facilitating the organized fluid formulations. The microfluidic device for producing W/O/W double emulsions consists of two tapered capillaries, one for injection and the other for collection (Fig. S1). The typical diameters of the injection capillary and the collection capillary were 50 μm and 180 μm , respectively. These two cylindrical tubes were inserted into a square capillary and coaxially aligned.

Synthesis of PU elastomer microshell particles: To generate emulsions, each fluid was loaded into a glass syringe (Hamilton Gastight, USA) that was fitted with a 20G luer-stub. The luer-stub was connected with a polyethylene (PE) tube having an outer diameter of 1.32 mm (PE-5, Scientific Commodity, USA). Typical flow rates of inner (Q_{IF}), middle (Q_{MF}) and continuous (Q_{OF}) fluid are 500, 650 and 2000 $\mu\text{L}\cdot\text{h}^{-1}$. The flow rate of each fluid was precisely controlled with syringe pumps (Pump 11 Elite, Harvard Apparatus USA). The double emulsion drops are collected in 80 mM NaCl solution. Volatile solvents in the oil phase are removed at room temperature. The PEGDA in the core and PU precursor in the shell are polymerized by irradiating UV light for 1 min (500 Watt, A&D CO., Korea).

Shell deformation under osmotic pressure: To confirm how the presence of hydrogel in the core affects the PU shell deformation behavior, the PU elastomer microshell particles whose core is filled with water or hydrogel, respectively, were produced. Then, 0.1 vol% of particles were dispersed in the aqueous solution of NaCl at room temperature. For both of dispersions, the concentration of NaCl was exactly tuned with 2 M. On applying the osmotic pressure, the shell deformation was monitored with the time interval of 10 s via a bright-field microscope. The surface topology of the deformed shell was also observed a scanning electron microscope (MIRA3, Tescan) at an acceleration voltage of 15 kV.

Characterization: Generation of drops in the micro-capillary device is monitored with a high speed camera (Phantom Miro EX2). The shape and morphology change of PU microshells are observed with an optical microscope (Axio Vert. A1, Carl Zeiss). To confirm the phase of core and shell, each phase is labelled with a fluorescence dye: the hydrogel core with FITC dextran ($70,000\text{ g}\cdot\text{mol}^{-1}$) and the shell with Nile red. Then, the phase is observed with a confocal laser scanning microscope (SP8 X STED, Leica). The modulus of PU precursors are measured with a universal testing machine (UTM, United Co., Model STM-10E).

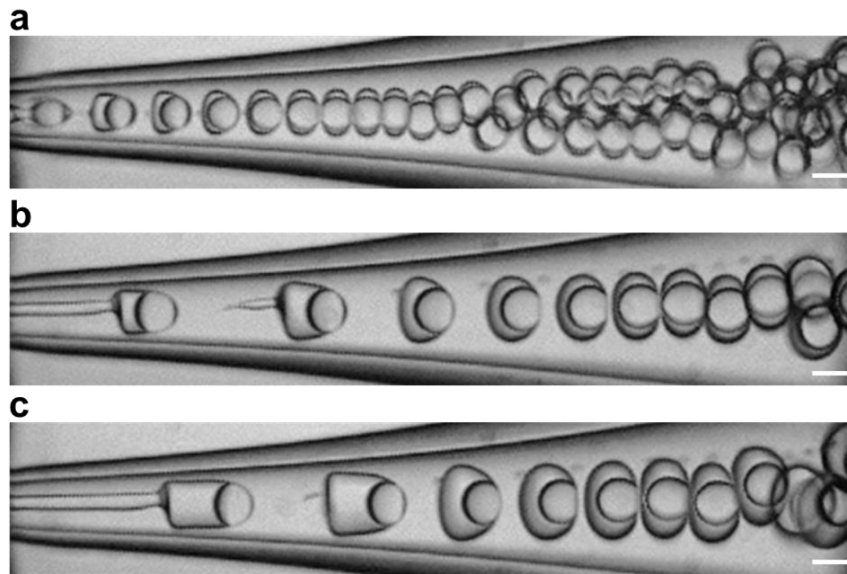


Figure S3. Control over the shell thickness of W/O/W double emulsion drops by scaling flow rates. (a) $Q_{IF}=500 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{MF}=650 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{OF}=2000 \mu\text{L}\cdot\text{h}^{-1}$, (b) $Q_{IF}=200 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{MF}=500 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{OF}=2000 \mu\text{L}\cdot\text{h}^{-1}$, (c) $Q_{IF}=200 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{MF}=900 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{OF}=2000 \mu\text{L}\cdot\text{h}^{-1}$. The scale bars are $100 \mu\text{m}$.

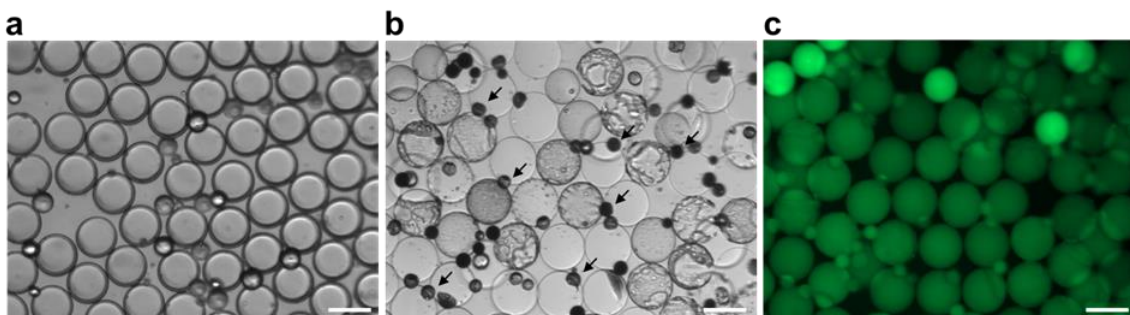


Figure S4. Induction of dewetting by polymerization. Optical microscope images of double emulsion droplets (a) before and (b) after polymerization. (c) Fluorescence microscopy image of microparticles containing Dextran (70K g/mol) in the core. The arrows indicate excess PG-b-PCL block copolymers attached to polymersome particles. Scale bars are $100 \mu\text{m}$.

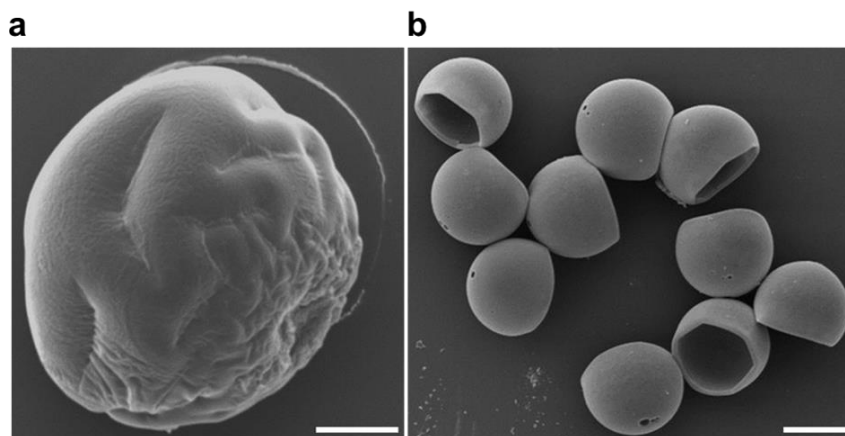


Figure S5. (a) SEM image of a PU elastomer microshell particle made with the high modulus PU (600 MPa). The scale bar is 10 μm . (b) SEM image of PU microshell particles after collapsing the spherical shell structure. The core of these shell particles is filled with water. The scale bar is 50 μm .