Supporting Information

Title: Self-Lubricating Organogels (SLUGs) with Exceptional Syneresis-induced Anti-sticking Properties Against Viscous Emulsions and Ices

*Chihiro Urata, Gary J. Dunderdale, Matt W. England, and Atsushi Hozumi**

Experimental

Materials

Sylgard® 184 silicone elastomer kit was purchased from Dow Corning Toray Co. Ltd. Toluene, *n*-hexane, *n*-octane, 2,2,4,4,6,8,8-heptamethylnonane (isocetane), *n*-docecane, *n*-tetradecane, and *n*-hexadecane, were purchased from Wako Pure Chemical Industries Ltd. *n*-Octadecyltrichlorosilane was purchased from Tokyo Chemical Industry Co, Ltd. Polydimethylsiloxane (silicone oil), polymethylphenylsiloxane (AR20), polymethylphenylsiloxane (CR100), Phenylmethylsiloxane-dimethylsiloxane copolymer (AS100), and phenylmethylsiloxane-dimethylsiloxane copolymer (AP100) were purchased from Sigma-Aldrich Co. Polymethylphenylsiloxane (TSF431) and polymethylphenylsiloxane (TSF437) were purchased from Momentive Co. All chemicals were used as received without further purification.

Preparation of PDMS-resin and organogels

PDMS-resin and various types of organogel were prepared by the following procedure (see Table S2 for the composition). First, 1 g of Sylgard 184 Base was mixed with *a* mL of an organic liquid phase1, *b* g of an organic liquid phase2, and 0.1 mL of Sylgard 184 curing agent; the solution was then vigorously mixed to obtain a homogeneous solution. The transparent solution was heated at 100 °C for 3 h in a Teflon® container/tray (perfluoroalkoxy copolymer resin, PFA), glass vial, or petridish to promote gelation. For the preparation of large samples, the compositions in the Table S2 were scaled up.

Swelling measurements

Swelling ratio of PDMS-resin for various liquids were obtained by comparing the original volume and estimated swollen volume, after being immersed in a solvent. We chose *n*-hexane as an extraction solvent because it shows high affinity for PDMS precursors and the resulting matrices, as well as has high volatility. First, pieces of PDMS-resin prepared from Sylgard 184 kit (about 10 mm × 6 mm × 1.5 mm), were washed by Soxhlet extractor for 48 hours using *n*-hexane to remove unreacted silicones from the PDMS-resin. The pieces were then dried in an oven for 48 hours at 100 °C to remove the *n*-hexane completely. Each piece was then immersed in 3 mL of organic liquid(s) and shaken at 100 rpm for 4 days. After the swelling procedure, the pieces were wiped to remove any residual liquid and weighed. This weight was then converted to a volume by multiplying with the density of the each swelling liquid. The swelling ratio was calculated using the following formula. Measurements were performed at least 3 times for each sample.

Swelling ratio (S, %) = $(V/V_0) \times 100$

V_0: initial volume of PDMS-resin

V: V_0 + uptaken volume of organic liquid

Syneresis behavior measurements

Syneresis behavior of organogels was investigated by monitoring their mass over time. Before weighing, gels were wiped dry of liquid using adsorbent tissue paper. The weight loss of the organogels was calculated as following formula. Measurements were performed at least 3 times for each sample.

Weight loss (%) = $((100-W_t)/W_0) \times 100$

W_t= Weight of the organogels after the wipe dry

W_0= Initial weight of the organogel

Observation of droplet shape on the syneresis organogels surface

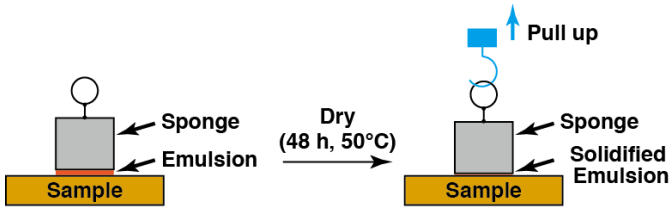
Static contact angles and shapes of water droplets were observed using a CA goniometer (Kyowa Interface Science, model CA-V150). A 5μL water drop was dispensed onto the organogels, and observed at various times. All measurements were performed at least 5 times for each sample.

Measurement of water droplet velocity on inclined surfaces

Water droplet and various emulsions (50 μL) were set on a sheet of organogel (100 mm × 100 mm) inclined at 30°. The average velocity was estimated using the total time to cross 100 mm of the sheet. Measurements were performed at least 5 times for each sample.

Adhesion force measurement of solidified emulsions

Several emulsions were interposed between samples and a sponge equipped with a hook (30 mm × 30 mm) then the dried for 48 hours at 50 °C. After the emulsion had solidified, the hook was pulled up using a texture analyzer (CT3-4500, Brook field) in order to obtain the adhesion strength. Measurements were performed at least 5 times for each sample.

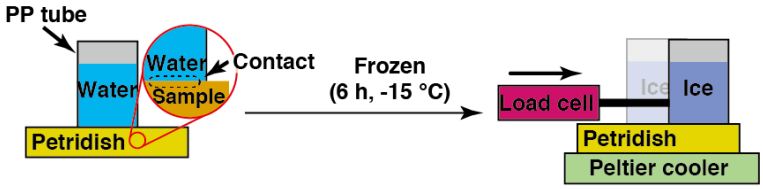


Thermo-responsive syneresis behavior of the organogels

Organogels coated on petridishes (φ: 90 mm) were cooled to -15 °C for 6 hours. After the incubation, the petridishes were warmed back to room temperature (r.t.). Measurements were performed at least 5 times for each sample.

Ice adhesion test

Ice adhesion test was performed by a simple and conventional method demonstrated by many researchers (references #4 l)-n) and #10). Water (15 mL) was added to a polypropylene tube (φ: 24 mm, h: 55 mm) on the samples coated on the petridish and water was frozen at -15 °C in the freezer for 6 hours. The test sets were transferred to the home-made ice adhesion strength-tester, which was equipped with a peltier cooling stage. The ice adhesion strength was measured by pushing the ice pillar with a stainless pole with a load cell. Measurements were performed at least 15 times for each sample.



Ice sliding test

Water (50 mL) was added into a polypropylene tube (φ: 32 mm, h: 80 mm) on the organogel-coated petridishes set on a rotating stage. Water was frozen by cooling it to -15 °C in the freezer for 6 hours and test sets were then inclined to 20°.

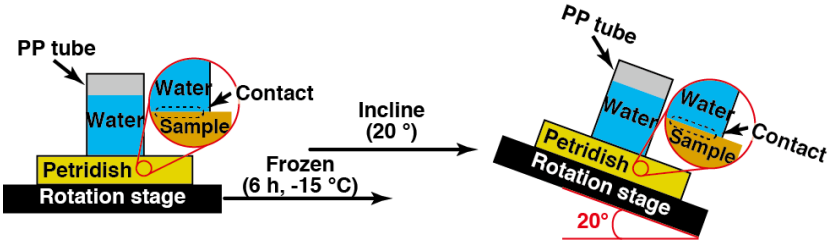


Table S1. Physico-chemical properties of the organic liquids used in this study.

Liquid name	MW (g/mol)	Viscosity (mPa•s)	Density (g/cm^3)	Boiling point (° C)	Melting point (° C)	Surface tension (dyn/cm)	Miscibility for PDMS precursor	Swelling ratio (S, %)	Standard deviation (–)	Class
n–Hexane	86.17	0.32	0.66	69	–95	18.5	YES	2.45	0.0072	I
n–Octane	114.23	0.508	0.702	126	–57	21.82		2.31	0.0404	
Toluene	92.14	0.55	0.866	111	–95	28.4		2.24	0.0086	
n–Decane	142.28	0.86	0.731	174	–30	23.6		2.12	0.0057	
Isocetane	226.44	3.299	0.784	247	102	24.32		1.96	0.0079	
n–Dodecane	170.33	1.3791	0.746	216	–12	23.35		1.94	0.0080	
Polydimethylsiloxane (silicone oil)	770	5	0.913	N/D	–55	19.7		1.93	0.0135	
n–Tetradecane	198.39	2.0883	0.763	253	6	26.56		1.73	0.0075	
Polymethylphenylsiloxane (AR 20)	350–450	20	1.01	N/D	N/D	N/D		1.68	0.0099	
n–Hexadecane	226.44	3.08	0.775	N/D	16–19	27.4		1.52	0.0072	II
Polymethylphenylsiloxane (CR 100)	N/D	100	1.07	> 250	< –60	N/D		1.41	0.0892	
Phenylmethylsiloxane–dimethylsiloxane copolymer (AS 100)	N/D	100	0.995	N/D	< –60	N/D		1.37	0.0032	
Polymethylphenylsiloxane (TSF 431)	N/D	100	0.99	> 250	< –70	21.3		1.33	0.0126	
Polymethylphenylsiloxane (TSF 437)	N/D	22	1.02	N/D	N/D	N/D	No	1.50	0.0948	III
Octadecyltrichororosilane	247.67	N/D	1.07	229	23	N/D		1.14	0.0235	
Phenylmethylsiloxane–dimethylsiloxane copolymer (AP 100)	2000–2100	100	1.06	>350	< –30	24.5		1.10	0.0080	
Water	18.02	0.8	1	N/D	0	72.8		1.00	0.0023	

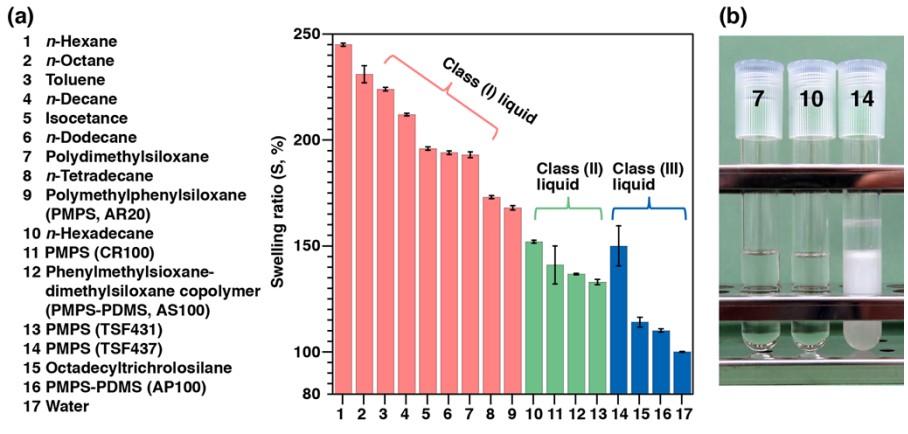


Fig. S1. Compatibility of PDMS-resin toward various organic liquids phases. (a) Swelling ratio of PDMS-resin toward several types of organic liquids and water. (b) Typical appearance of precursor solutions after mixing PDMS-precursor with polydimethylsiloxane (7, class (I) liquid), *n*-hexadecane (10, class (II) liquid), and TSF437 (14, class (III) liquid).

Table S2. Compositions of the precursor solution applied in this study.

Sylgard		Liquid 1		Liquid 2		Volume percentage of organic liquid
Base (g)	Curing agent (mL)	Type of liquid	a, mL	Type of liquid	b, mL	α, %
1	0.1	1–13	0.5–30	–	–	50, 100, 150, 300, 600, 1200, and 3000
1	0.1	8	0.3–2.7	10	0.3–2.7	300
1	01	5	2.25	15	0.75	300
1	0.1	9	0.3–2.7	14	0.3–2.7	300

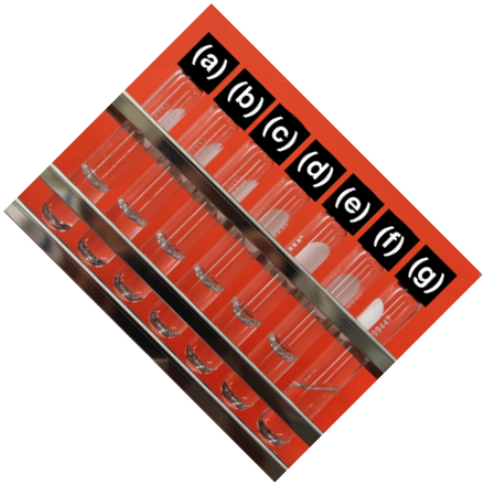


Fig. S2. Typical appearance of organogels (organic liquid: *n*-decane, α: a=50, b=100, c=150, d=300, e=600, f=1200, g=3000). The samples were tilted at 45° to emphasis on the sol state of g=3000.

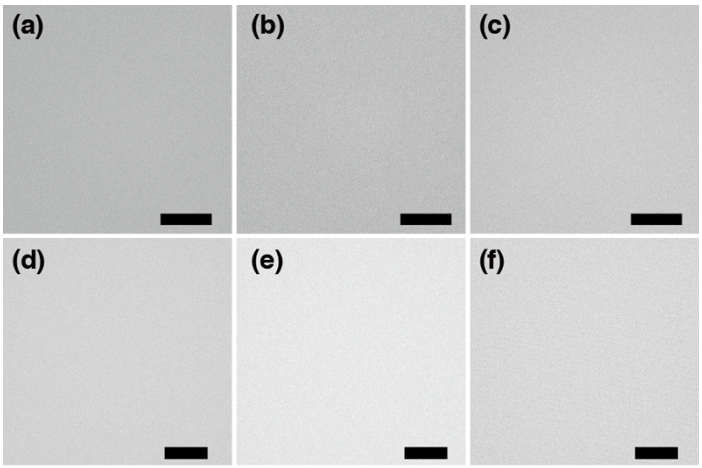


Fig. S3. SEM images of (a,d) PDMS-resin, (b,e) non-syneresis organogel (AR20, α=300%), and (c,f) syneresis organogels (TSF431, α=300%). Scale bar in the upper images are 30 μm and lower images are 5 μm The organic phase in the sample (b,e) and (c,f) were extracted with *n*-hexane before the SEM observation.

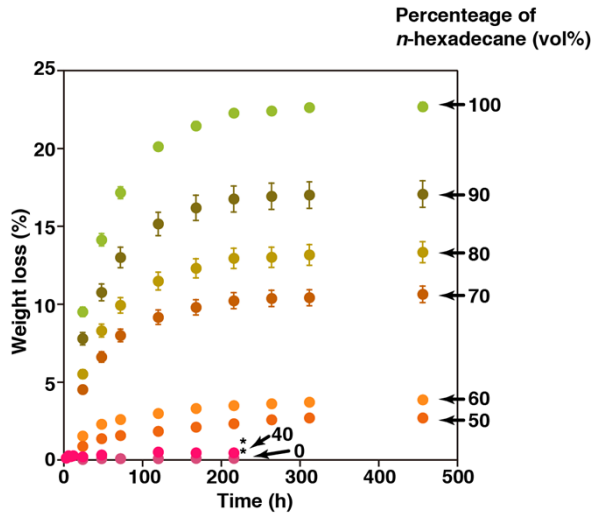


Fig. S4. Syneresis rates of organogels prepared with mixed organic phases (different volume percentage of *n*-hexadecane to *n*-tetradecane, * indicates end of the measurements).

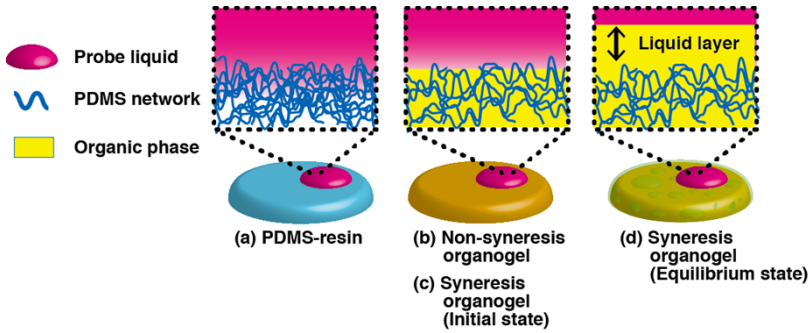


Fig. S5. Interfacial images of the samples (a: PDMS-resin, b: non-syneresis organogel, c: syneresis organogel in the initial state and d: syneresis organogel in the equilibrium state).

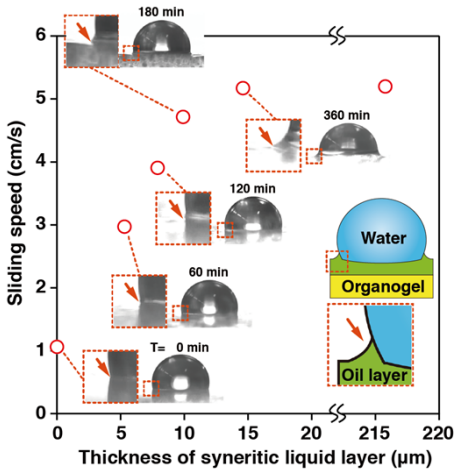


Fig. S6. Changes in dynamic dewetting behavior of water drops on the syneresis organogel (prepared with TSF431 as an organic phase) as a function of thickness of syneresis liquid layer. Inset images: time lapse images of a water droplet on the syneresis organogel (number on each water drop image indicates the elapsed time (min) after syneresis) and schematic image of the "wetting ridge".

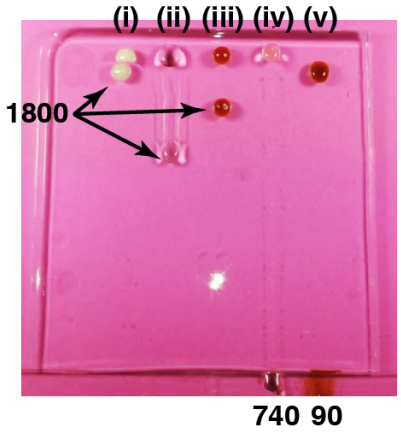


Fig. S7. Time lapse image of the flowing of emulsions (i: mayonnaise, ii: liquid glue, iii: ketchup, iv: honey, v: worcester source) on the non-syneresis organogel (prepared with AR20 as an organic phase) surface inclined at 30°. (Numbers in the image indicate the position of the emulsions at the time (sec). 2 images were overlaid to create the composite image displayed.)

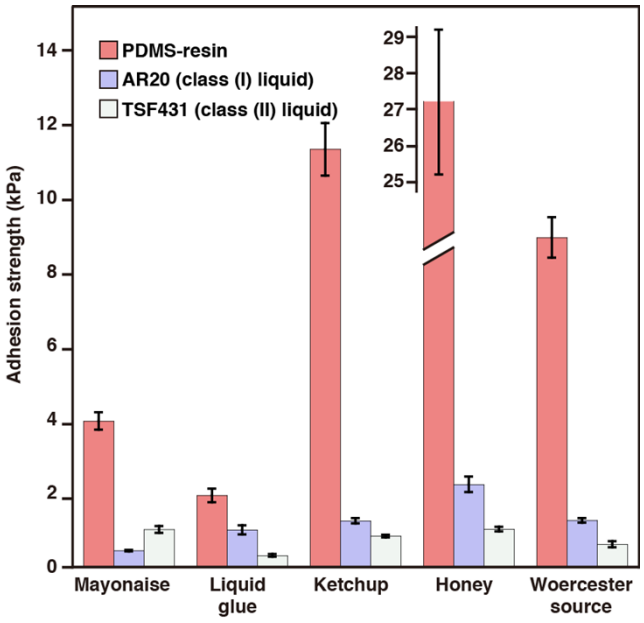


Fig. S8. Adhesion strength of the solidified emulsions on the PDMS-resin, and organogels prepared with AR20 (class (I) liquid) and TSF431 (class (II) liquid).

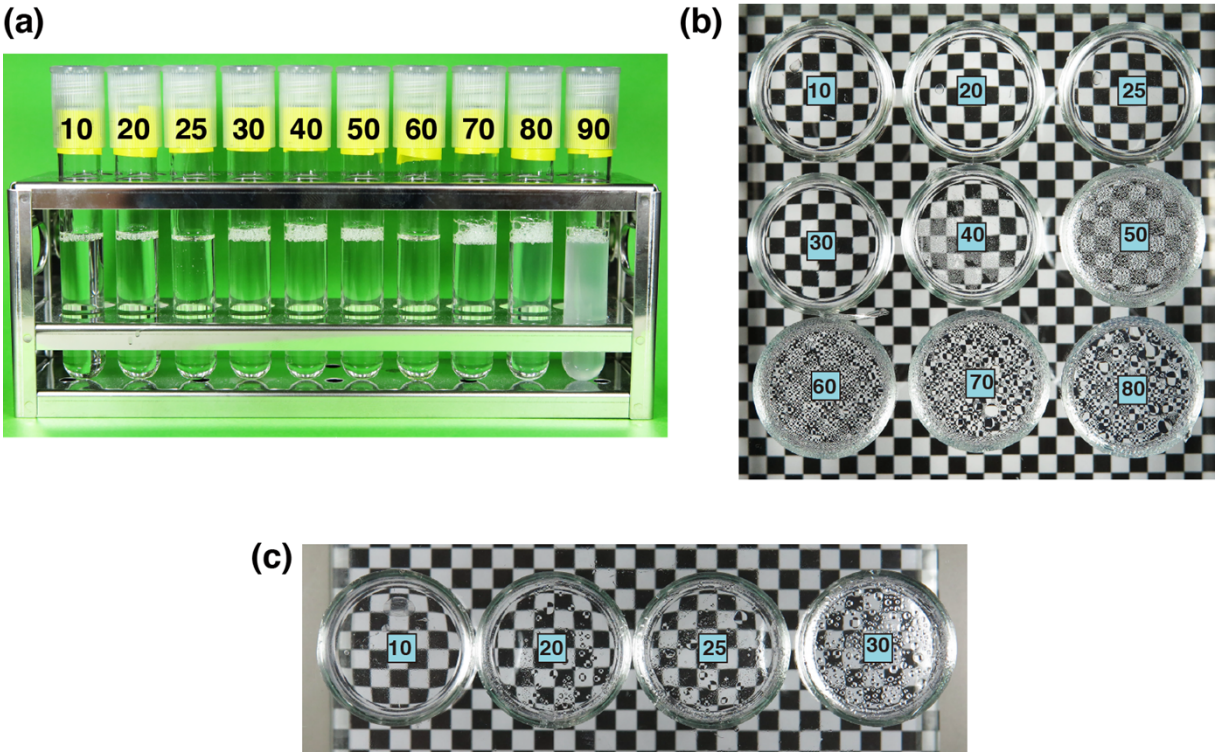


Fig. S9. (a) Appearance of precursor solution prepared with mixtures of AR20 (class (I) liquid) and TSF437 (class (III) liquid) as organic phases in various proportions. (b) Syneresis behavior of organogels at r.t. (c) Syneresis behavior of organogels after incubation for 6 hours at -15 °C. Number on the vials and organogels indicate the volume percentage of TSF437.

Movie S1. Time-lapse movie of syneresis behavior of organogels prepared with AR20 (class (I) liquid) and TSF431 (class (II) liquid) (Replay speed: ×900).

Movie S2. Time-lapse movie of differences in slippery properties of emulsions (Replay speed: ×10) on the organogel prepared with TSF431 (class (II) liquid).

Movie S3. Time-lapse movie of differences in slippery properties of emulsions (Replay speed: ×120) on the organogel prepared with AR20 (class (I) liquid).

Movie S4. Time-lapse movie of the formation of superhydrophobic organogels surfaces prepared with isocetane (class (I) liquid) and *n*-octadecyltrichlorosilane (class (III) liquid) (Replay speed: ×370).

Movie S5. Behavior of water droplets on the superhydrophobic organogel surface shown in Movie S4 (Replay speed: ×1).

Movie S6. Spontaneous motion of an ice pillar formed on an organogel prepared with a mixture of AR20 (class (I) liquid) and TSF431 (class (II) liquid) (Replay speed: ×300).