"Big Dipper" Dynamic Contact Angle Curves for Pt-Cured PDMS on a Thermal Gradient: Interrelationships of Hydrosilylation, Si-H Autoxidation and Si-OH Condensation to a Secondary Network.

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Supporting Information

Calculation S1. Penetration depth (d_p) for Germanium (Ge) crystal

$$L = d_p = \frac{(\lambda)/n_c}{2 \times \pi \times [\sin^2 \theta - (\frac{n_s}{n_g})^2]^{1/2}}$$

L = Diffusion path length = d_p = effective penetration depth

λ = peak wavelength

θ = angle of incidence

n_g = crystal refractive index

n_s = PDMS refractive index

The Si-OH group has an absorbance peak at ~3500 cm^{-1} (wavenumbers) which corresponds to λ = 2857 nm (wavelength). For the Smart iTR instrument the angle of incidence is θ = 45°.

For the germanium crystal, n_g = 4.0 for λ = 2857 nm = 2.9 μm which means:

$$L = d_p = \frac{(2857 \text{ nm})/4}{2 \times \pi \times [\sin^2 45^\circ - (1.4/4)^2]^{1/2}}$$

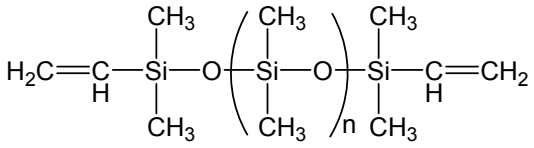
= 185 nm

The Si-H group has an absorbance peak at ~2150 cm^{-1} (wavenumbers) which corresponds to λ = 4651 nm (wavelength). So, the penetration depth (d_p) for the Ge crystal

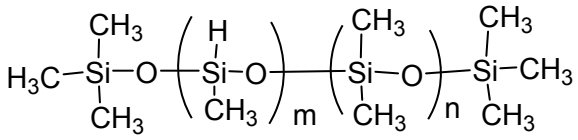
d_p = 301 nm

Calculation S2: Calculation of mole ratios for the different base:crosslinker systems.

a. Vinyl terminated polydimethylsiloxane (MW 28 kDa)



b. Methylhydrosiloxanedimethylsiloxane copolymer, trimethylsiloxy terminated [crosslinker] (MW 900-1200 Da, approximated to 1 kDa, $SiO(H)(CH_3)$ 50-55 mole%)



Number of repeat units of $SiO(CH_3)_2$ in 'a' = 377

Number of repeat units of $SiO(H)CH_3$ in 'b' = 7 (based on 1 kDa molecular weight and 52.5 mol% of $SiO(H)CH_3$)

<u>For 10:1 PDMS coatings:</u>

Hence, ratio of $SiO(CH_3)_2$ to $SiO(H)CH_3$:

$$377 \times \frac{10}{28000} : 7 \times \frac{1}{1000}$$

$$= \mathbf{19}:\mathbf{1}$$

Ratio of $SiO(CH_3)_2CH{=}CH_2$ to $SiO(H)CH_3$:

$$2 \times \frac{10}{28000} : 7 \times \frac{1}{1000}$$

$$= \mathbf{1}:\mathbf{10}$$

2 repeat units of $SiO(CH_3)_2CH{=}CH_2$ is approximate, taking into account end groups of 'a'.

Table S1. Temperature and heating times for S-PDMS and Pt-PDMS coverslip coatings cured on thermal gradients.[a]

Sample ID[c,d]	Temperature (°C), time (h) S1[b]	Temperature, (°C), time (h) S2[b]	Temperature (°C), time (h) S1[b]	Temperature, (°C), time (h) S2[b]
S-PDMS(45) Pt-PDMS(45)	45, 96	45, 48	-	-
S-PDMS(140) Pt-PDMS(140)	140, 48	140, 24	-	-
S-PDMS(45-140) Pt-PDMS(45-140)	45, 24	45, 12	140, 24	140, 12
S-PDMS(45-140) Pt-PDMS(45-140)	45, 48	45, 24	140, 48	140, 24
S-PDMS(45-140) Pt-PDMS(45-140)	45, 96	45, 48	140, 96	140, 48

a. Processing conditions are the same for S-PDMS and laboratory prepared Pt-PDMS (Experimental).
b. S1 and S2 refer to coverslip sides.
c. (45) and (140) indicate cure temperature.
d. Gradients are designated S-PDMS(45-140) or Pt-PDMS(45-140).

Table S2: XPS area calculation for Si 2p peak.

Binding energy (eV)	Area[1]	Area %*
101.5	19221	96
102.5	800	4

Area[1] total: 20021
Area[2] : 20139
% area difference = 0.6%

Binding energy (eV)	Area[1]	Area %*
101.5	18836	96
102.5	883	4

Area[1] total: 18255
Area[2] : 18419
% area difference = 0.9%

[1]Determined by CASAv 2.3.16 PR 1.6
[2]Determined by Avantage 4.4

$$*Area\% = \frac{Area\,(1)+Area\,(2)}{Area\,(total)}$$

Table S3. Comparison of θ_A and θ_R for Pt-PDMS(45-140) coatings on coverslips prepared at two different times. The θ_A is always high irrespective of cure conditions but the θ_R increases as the cure time increases.

	θ_A	θ_R
Ist set of DCA samples		
Pt-PDMS(45-140)-24/12	116	43
Pt-PDMS(45-140)-48/24	113	55
Pt-PDMS(45-140)-96/48	116	68
2nd set of DCA samples		
Pt-PDMS(45-140)-24/12	92	28
Pt-PDMS(45-140)-48/24	100	45
Pt-PDMS(45-140)-96/48	105	60

Table S4. Average θ_A and θ_R for S-PDMS and Pt-PDMS coatings measured by drop addition-withdrawal (A-W) method at different cure times that correspond to images in **Figures 9, S8** and **S9**.

Sample designations	Cure time	θ_A	θ_R	θ_Δ
S-PDMS(45)	96 h	125	**45**	80
S-PDMS(140)	48 h	110	92	18
S-PDMS(**45**-140)	24 h	117	**44**	73
S-PDMS(45-**140**)	24 h	117	105	12
S-PDMS(**45**-140)	48 h	113	**47**	66
S-PDMS(45-**140**)	48 h	113	107	6
S-PDMS(**45**-140)	96 h	113	**48**	65
S-PDMS(45-**140**)	96 h	113	106	7
Pt-PDMS(45)	96 h	122	**47**	75
Pt-PDMS(140)	48 h	110	100	10
Pt-PDMS(**45**-140)	24 h	114	**51**	63
Pt-PDMS(45-**140**)	24 h	114	100	14
Pt-PDMS(**45**-140)	48 h	114	**52**	62
Pt-PDMS(45-**140**)	48 h	114	99	15
Pt-PDMS(**45**-140)	96 h	112	**53**	59
Pt-PDMS(45-**140**)	96 h	112	96	16

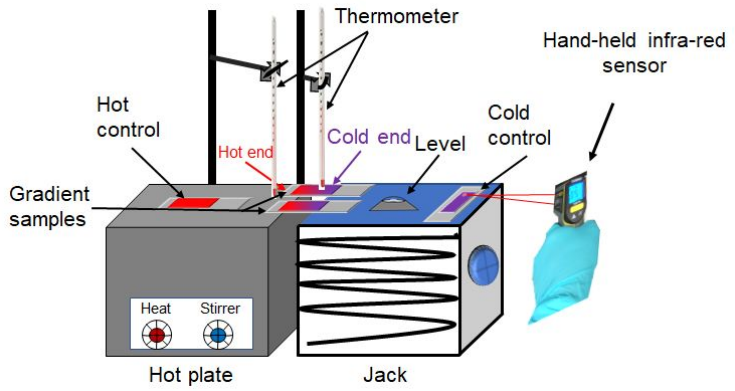


Figure S1. Experimental apparatus for the preparation of coatings cured in a 45 – 140 °C thermal gradient.

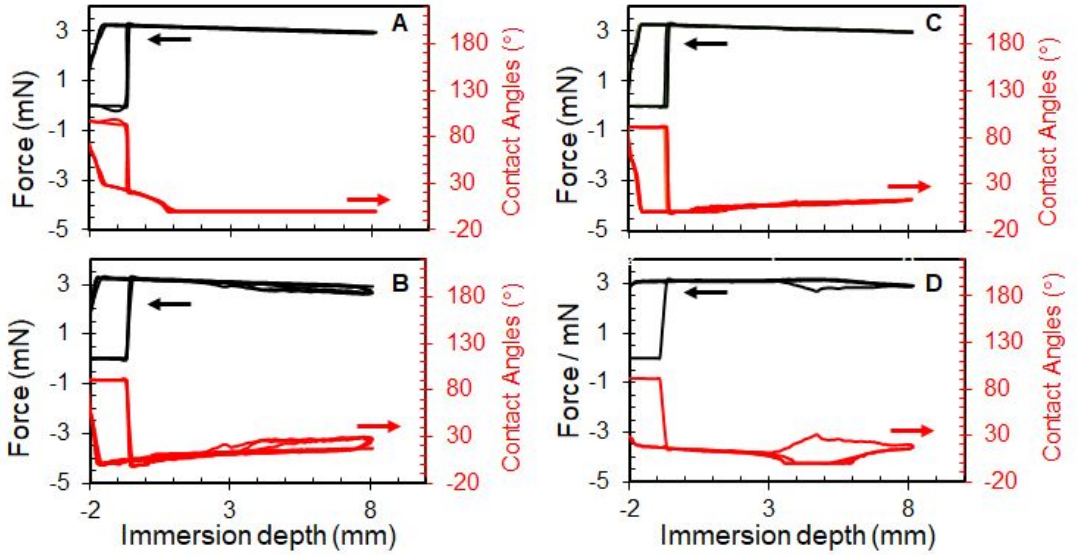


Figure S2. Three cycles comprising pre- and post-water check by DCA with a flamed glass slide for S-PDMS(45-140) and Pt-PDMS(45-140) gradients (T_{cure}:48/24 h). Black: force distance curves (fdc), Red: contact angles. **A**, pre-check; **B**, post-check of S-PDMS(45-140) gradient, **C**, pre-check; **D**, post-check of Pt-PDMS(45-140) gradient. A detailed procedure has been published: Uilk, J. M. M., A. E.; Fox, R. B.; Wynne, K. J., Hydrosilation-cured poly(dimethylsiloxane) networks: Intrinsic contact angles via dynamic contact angle analysis. *Macromolecules* **2003,** *36* (10), 3689–3694.

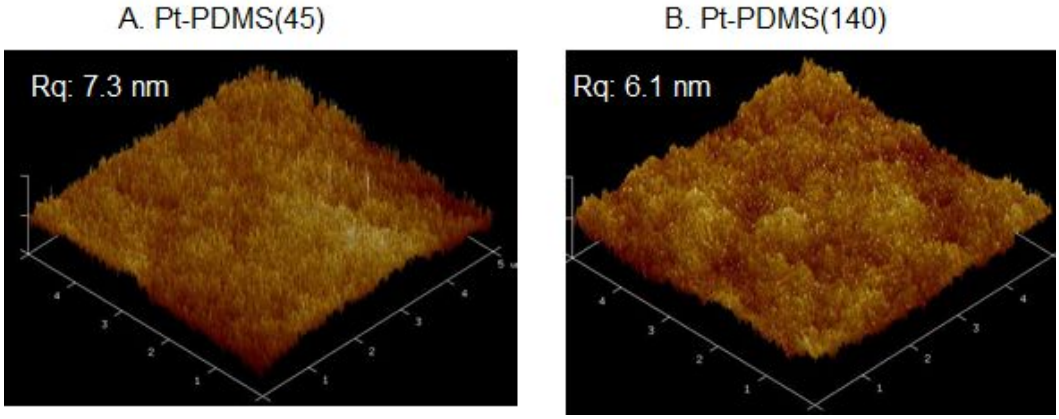


Figure S3. Tapping Mode Atomic Force Microscopy 3D height images for **A**. Pt-PDMS(45) (cured 96 h) and **B**. Pt-PDMS(140), cured 48 h. r_{sp} was 0.8. R_q is shown in the images. Z= 200 nm.

Peak deconvolution

The peak area was calculated using smart background correction. The area difference between two different area measurement programs, Avantage and CASA software, were in agreement within <1%. The difference in area when the broad Si 2p peak was fitted with just one peak (light purple within red curve) was found to be >3% (**Figure S4**). This comparison supports the existance of two peaks from two Si species in the system as shown in **Figure 3**, as the area match was within 1%.

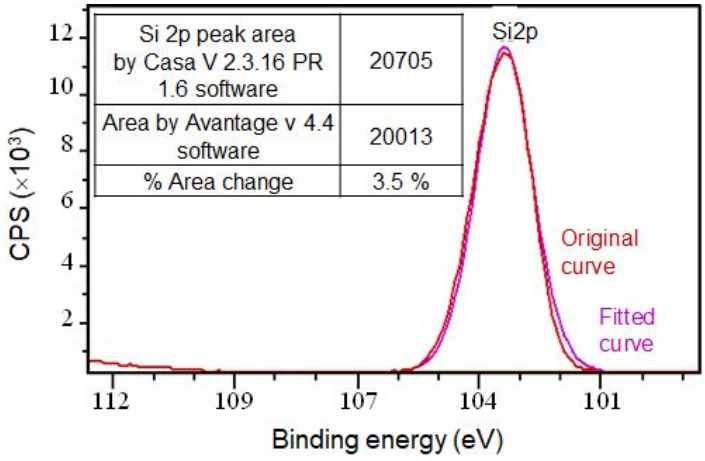


Figure S4. Si 2p peak (red) fitted with only one peak (purple curve). Inset shows the area under Si 2p peak calculated by using Casa and Avantage software. The two peak fit shown and discussed in the text is a better fit (**Figure 3**).

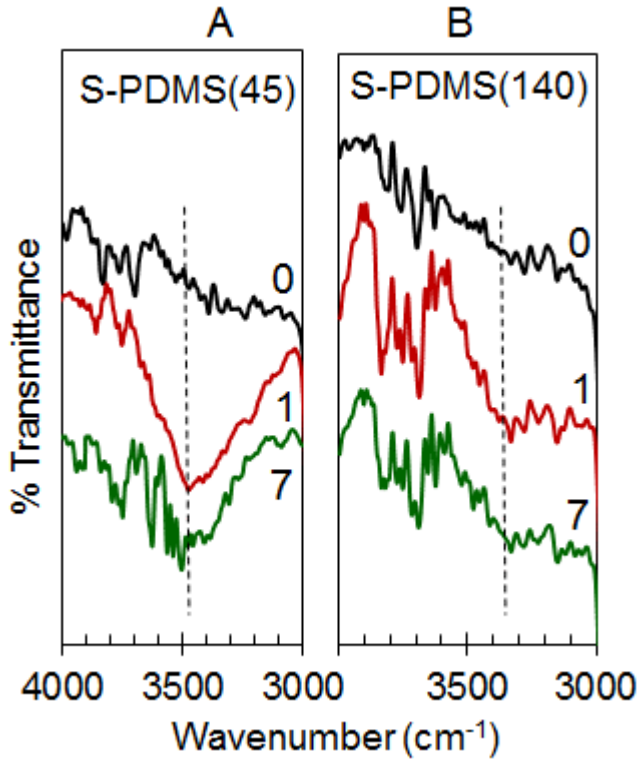


Figure S5. ATR-IR spectra for S-PDMS coatings prepared on microscope slides uniformly cured at 45 or 140 °C. Absorptions for Si-OH at ~3450 cm^{-1} before (0) and after immersion cycles **1** and **7**. Each cycle consisted of immersion in water for 10 min followed by drying (1 min) in N_2 and drying in air for 6 h.

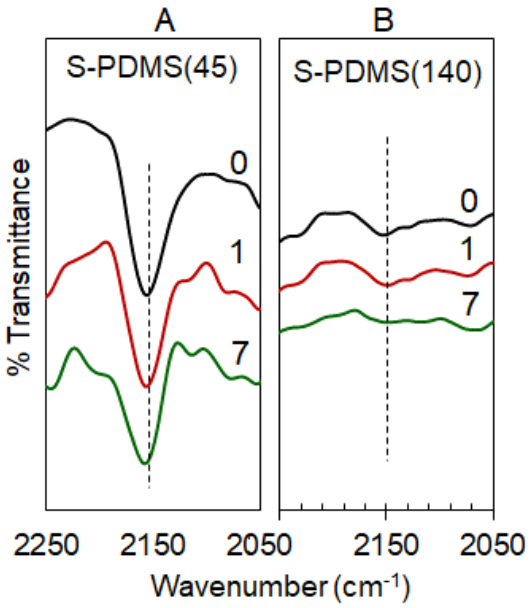


Figure S6. ATR-IR spectra of S-PDMS coatings prepared on microscope slides uniformly cured at 40 or 140 °C. Absorptions for Si-H at ~2150 cm^{-1} before and after immersion in water. Cycle numbers 1 and 7 are indicated. Each cycle consisted of immersion in water for 10 min followed by drying (1 min) in N_2 and drying in air for 6 h.

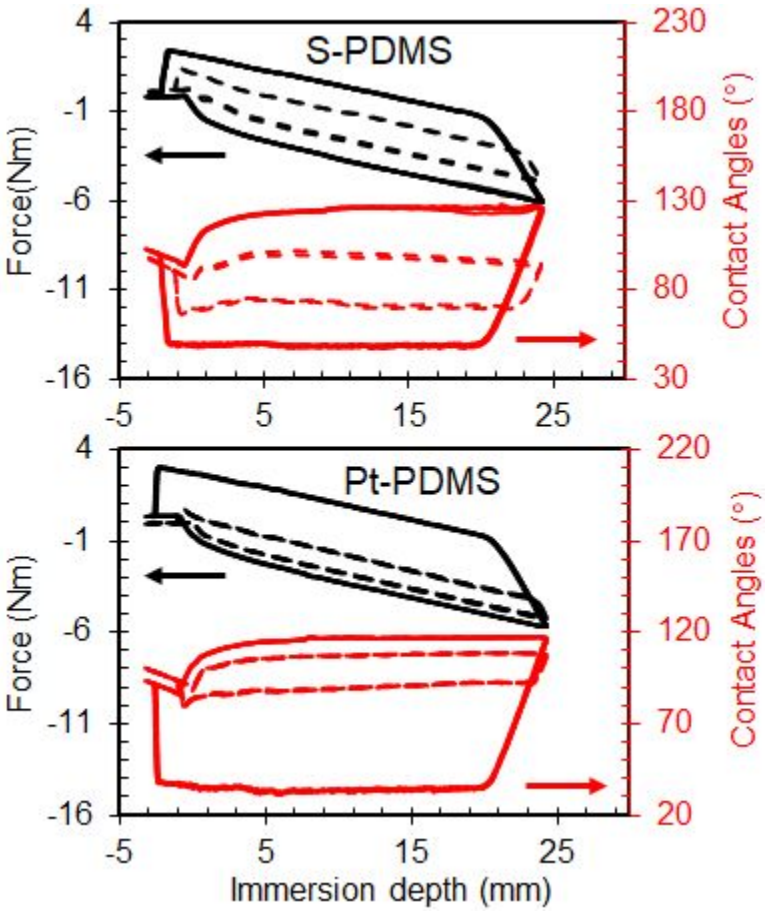


Figure S7. DCA data: **A,** S-PDMS(45) (solid line) and S-PDMS(140) (dashed line); **B**, Pt-PDMS(45) (solid line) and Pt-PDMS(140) (dashed line). Four DCA and force-distance curves in sequence are superposed.

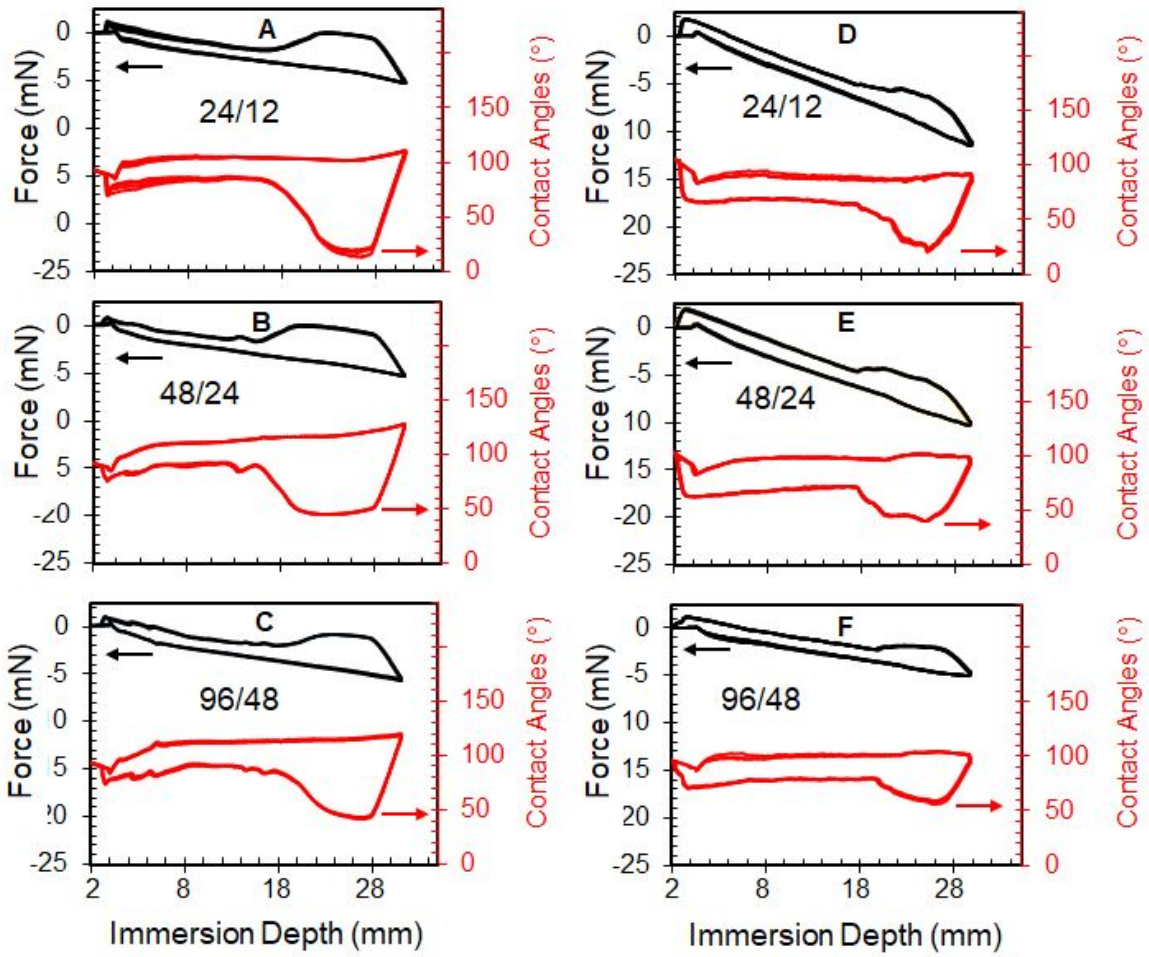


Figure S8. Force distance curves (fdc's, black) and contact angles (degrees, red), for gradients: **A**, S-PDMS(45-140)-24/12; **B**, S-PDMS(45-140)-48/24; **C**, S-PDMS(45-140)-96/48; **D**, Pt-PDMS(45-140)-24/12; **E**, Pt-PDMS(45-140)-48/24; **F**, Pt-PDMS(45-140)-96/48. Curves are superposition of four cycles.

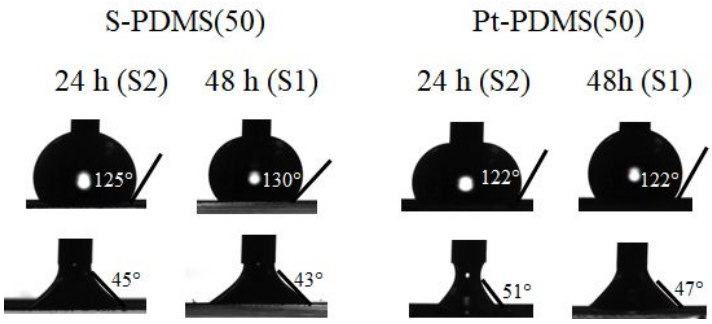


Figure S9. θ_A and θ_R for S-PDMS(50) and Pt-PDMS(50) coatings on coverslips. The coverslips were coated on one side (S2) cured at 50 °C for 24 h, contact angles were taken. Then the other side (S1) of the coverslips were coated and cured for 24 h and contact angles were determined.

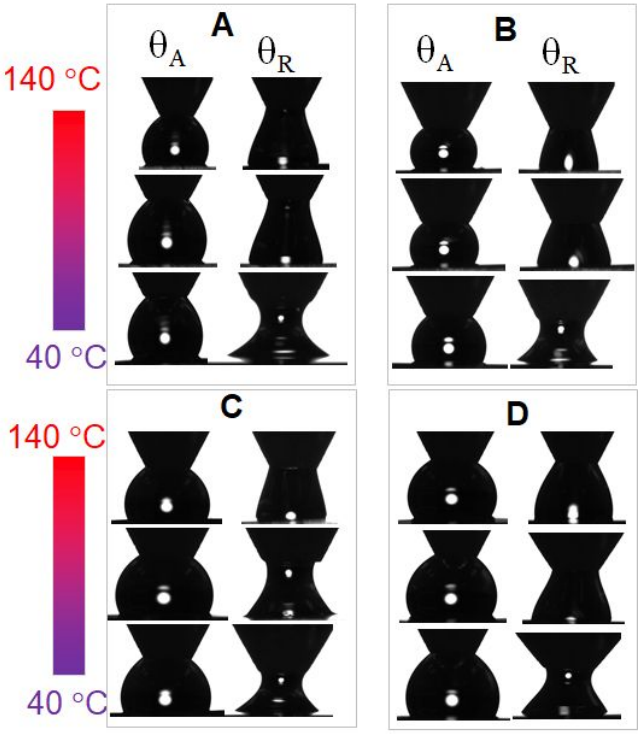


Figure S10. Water drop addition/withdrawal images: **A,** S-PDMS(45-140) (T_{cure}: 24 h); **B**, S-PDMS(45-140) (T_{cure}: 96 h) **C**, Pt-PDMS(45-140) (T_{cure}: 24 h); **D**, Pt-PDMS(45-140) (T_{cure}: 96 h).

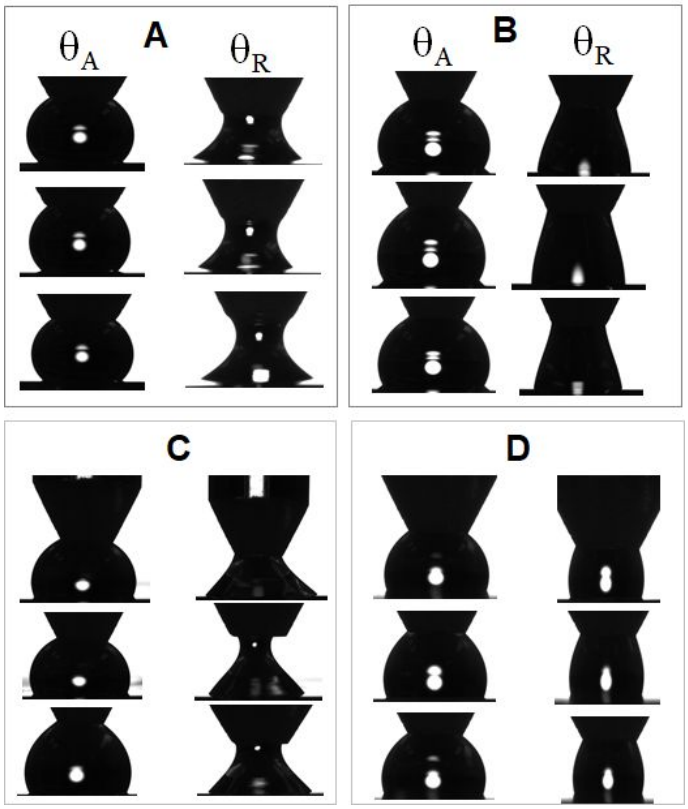


Figure S11. Water drop addition/withdrawal images for controls: **A,** S-PDMS(45); **B**, S-PDMS(140); **C**, Pt-PDMS(45) and **D**, Pt-PDMS(140). One-sided coatings were cured on microscope slides at uniform temperatures.

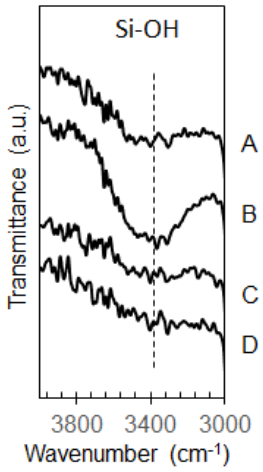


Figure S12. ATR-IR spectra: One year old samples of **A**, S-PDMS(25) and **C**, S-PDMS(100); **B** and **D** are after immersion of the respective coatings in water.