Low interfacial-toughness self-segregating thermoset for large-scale ice-release coating application.

(Supplementary Information)

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Materials and methods

Material

FM4411 (bicarbinol functional PDMS with a OH equivalent weight of 500 g/eq [Mn = 1,000 g/mol]) was provided by Japan New Chisso and Desmodur Z4470 BA (isophorone diisocyanate [IPDI] in butyl acetate [BA]) was provided by Covestro. Methyl-n-amyl ketone (MAK), ethyl-3-ethoxypropionate (EEP), 2,4-pentanedione and dibutyltin diacetate (DBTDAc) were obtained from Sigma-Aldrich. Placcel 305 (hydroxy-functional polycaprolactone with a OH equivalent weight of 180 g/eq) was obtained from Daicel and MCR-C12 (mono-amino functional PDMS with a NH_2 equivalent weight of 1000 g/eq [Mn = 2,000 g/mol]) was purchased from Gelest. Aluminum (bare aluminum [A], alloy 3003 H14) substrates were obtained from Q-panel.

Coating preparation

Two series of coating formulations were prepared. Coatings prepared with FM4411 (referred as C-PDMS) were designed in a way where the total PDMS content represents 5, 8, 10 or 12 wt.% of the total solids contents (PDMS + IPDI + Polyol) of the coating system. Coatings prepared with MCR-C12 (referred as A-PDMS) were designed in a way where the total PDMS content represents 5 wt.% of the solid contents (PDMS + IPDI + Polyol). In all of these formulations, the NCO:OH ratio was constantly kept at 1.5:1.0. Before use, DBTDAc was dissolved at 1 wt.% into MAK, and the amount of this solution added to this formulation was calculated as such that DBTDAc corresponded to 0.075 wt.% of the solid content (PDMS + IPDI + Polyol). 2,4-pentanedione was added in an amount corresponding to 10 wt.% of the solid content to reduce the catalytic activity of DBTDAc during the mixing step and avoid premature gelation. Additionally, the ratio of solvents EEP/MAK/BA was constantly kept at 45/13/42 through all formulations.

All components except Desmodur Z4470 BA were added at the same time into a 20 mL vial and mixed 2 min at 800 rpm using a stirring plate. Then the Desmodur Z4470 BA was added, and the mixture was stirred for an additional 2, 3 or 4 h at 800 rpm using the stirring plate. Three examples of the formulations are presented Table S1 displaying the exact weights used for each material. The presented weights have been calculated using a Desmodur Z4470 BA containing 68.3 wt.% of IPDI (NCO equivalent weight of 242.35 g/eq) as solid content. Additionally, a coating containing 0% of PDMS, referred to as PU control, was prepared using the same protocol with the exception that the NCO:OH ratio was kept to 1.1:1.0 and no EEP was used. Overnight formulations consist in two steps reactions: first the PDMS was left to react overnight with the isocyanate, and only then was the polyol added to the formulation and agitated for two more hours. An example of such formulation is given Table S2.

Coating formulations were then applied either on aluminum panels using wire application bars with wet thicknesses of 80 or 30 µm. The obtained coatings were then cured for 24h hours at ambient temperature before being exposed to 80 ˚C for 45 min. Bare smooth aluminum substrates were used only for experiments where the coated film needed to be peeled-off, and were cleaned with acetone and isopropanol prior application of the coatings. In any other cases, the aluminum substrate was first sandblasted on both sides using 100 µm aluminum particles and was then thoroughly rinsed under tap water and blown dry with nitrogen to remove any residues of sandblasting.

Table S1: Examples of formulation composition in weight

Material	10% C-PDMS	5% A-PDMS	PU control
Placcel 305	2.00 g	2.00 g	2.00 g
Desmodur Z 4470	6.78 g	6.12 g	4.34 g
FM 4411 or MCR-A12	0.74 g	0.34 g	0.0 g
TOTAL resin solids	7.37 g	6.62 g	5.04 g
EEP	2.20 g	1.98 g	0.00 g
2,4-pentanedione (10 wt%)	0.74 g	0.66 g	0.50 g
MAK (DBTDAc sol)	0.56 g	0.50 g	0.38 g
DBTDAc (0.075 wt%)	0.0056 g	0.0050 g	0.0038 g
MAK (complement)	0.08 g	0.08 g	0.02 g

Table S2: Example of overnight formulation composition in weight

Material	5% A-PDMS - O
Step 1 (overnight)	
Desmodur Z 4470	6.11 g
MCR-A12	0.34 g
EEP	1.99 g
MAK (DBTDAc sol)	0.50 g
DBTDAc (0.075 wt%)	0.0050 g
MAK (complement)	0.08 g
Step 2 (2h)	
Placcel 305	2.00 g
2,4-pentanedione (10 wt%)	0.66 g

AFM surface imaging

Imaging of the coating surface was performed using an Asylum Jupiter RX AFM in tapping mode and employing tips AC240TS-R3 (spring constant = 2, frequency = 72 KHz, tip radius = 7 nm) sold by Oxford Instruments. Calibration of the tip was performed using the thermal calibration and Bluedrive tuning (amplitude set at 2.00 V) options provided by the apparatus. Scans were performed using the following parameters: scan size 40 µm, points and lines 512, speed 0.70 Hz, integral gain 40, setpoint 1.20 V, drive amplitude 15 mW.

Force Mapping

Force mapping of the coating surface was performed using an Asylum Jupiter RX AFM in Fast Force Mapping mode and employing tips biosphere B20-CONT (spring constant = 0.2, frequency = 13 KHz, tip radius = 20 nm) sold by Nanotools. Calibration of the tip was performed using the thermal calibration

option provided by the apparatus. Scans were performed using the following parameters: scan size 20 µm, points and lines 512, Z rate 50 Hz, setpoint 120 nN and 1.20 V, force distance 400 nm. The conversion from force curves to modulus mapping was performed automatically by the AFM software using the Hertz-Sneddon model, and considering a sphere morphology with a radius of 20 nm. Given the limitations of the Hertz-Sneddon model with the experimental conditions and the lack of characterization of the real sphere dimensions, we kindly ask the reader not to consider the absolute values of modulus expressed during this experiment, but to rather focus their attention on the large variations of modulus observed across the surface, which represent a clear indicator of the presence of hard and soft phases across the surface.

Pi-FM

Photo-induced Force Microscopy (PiFM) was performed using a Vista One PiFM-Raman microscope from Molecular Vista, equipped with NCHR-Pt/Ir cantilevers (S/N: 100153L1576). The coated panels were cut into small discs using a precision cutter. Measurements were taken at a wavenumber of 1085 cm^{-1} corresponding to the middle of the range corresponding to Si-O-Si signals. Spectra were measured at different spots on the surface to scan different domains, and the data were processed using the VistaScan software.

Surface energy measurements

Surface energy measurements were performed using a Drop Shape Analyzer model DSA100S from Kruss. This apparatus was equipped with a water/diiodomethane dual dispenser used to deposit 2 µL droplets and record their contact angle. In tilting mode, the stage (flat at the beginning) was tilted of 15 ˚/min until reaching a final angle of 90 ˚.

Tensile experiment

Tensile experiments were performed using an Instron 5542 tensile apparatus. Coating samples were peeled-off from aluminum substrate by cutting them with a razor blade and inserting the razor blade between the coating and the substrate. The obtained free film was then cut in strips of 5 mm wide. The initial length of the sample (distance between jaws) was of 40 mm while the applied strain was of 5 mm/min.

SEM/TEM imaging

For this analysis, films were applied and cured on cleaned, smooth, aluminum panels (to reduce their adhesion) and peeled off using a sharp razor blade.

For electron microscopy observations, a film sample was embedded in LR White acrylic resin (Ted Pella Inc., Redding, California, USA) in flat silicon molds, covered to exclude air and polymerized at 55C for 24 hours. The embedded film was sectioned at 60-90 nm thickness on a RMC MT XL ultramicrotome (Boeckeler Instruments, Tucson, Arizona USA).

Sections for transmission electron microscopy (TEM) were collected on copper grids with a formvar-carbon supporting film (Ted Pella, Inc., Redding, California USA). Observation and imaging were performed on a JEOL JEM-2100 electron microscope (JEOL Inc., Peabody, Massachusetts, USA) operating at 200 kV. Brightfield images were obtained with a NanoSprint 15MKII bottom-mount camera (AMT Imaging, Woburn, Massachusetts USA).

Thicker ultramicrotome sections for scanning electron microscopy (SEM) were collected onto cylindrical aluminum SEM mounts (Ted Pella Inc., Redding, California, USA) and coated with a conductive layer of carbon in a high-vacuum evaporative coater (Cressington 208c, Ted Pella Inc., Redding, California, USA). Images were obtained with a JEOL JSM-7600F scanning electron microscope (JEOL USA Inc., Peabody, Massachusetts) operating at 2 kV.

Ice adhesion measurements

To test the interfacial toughness and ice adhesion of the coating, shear removal of ice was conducted following similar steps described previously.[35] The adhered ice was shaped and restricted in 3-D printed rectangular ABS molds of dimensions 0.6 cm x 1 cm (WxH). To get sufficient lengths to the toughness-domain region, the length of the molds was varied from 1 cm to 14 cm. Initially, coating samples were clipped on a fixture plate aluminum, and molds were placed on the coating surfaces while ensuring uniform testing conditions by choosing areas without visible defects (coatings made from A-PDMS with 80 µm thickness were almost free of defects, C-PDMS-80µm and A-PDMS-30µm presented a few visible defects that were avoided during testing, while C-PDMS-30µm presented too many defects to be avoided). The molds were filled with water in two steps (first half of their volume) and the plate was placed in the freezer set at -20°C for 50 min after the first filling step and for 15 min after the second filling. After complete freezing of the molds, the fixture plate with the coatings was taken out and secured onto the testing stage (cooled from the bottom at -20 °C). During the test, the temperature in the room was maintained at around 22 °C, and the relative humidity was recorded to vary between 40 and 60 %. In total, a minimum of three measurements per surface (N = 3) were taken, at each ice length and on two coating duplicates. The shear force required to dislodge the ice was recorded using a force gauge (IMADA ZTA-110) moving at a controlled velocity of 74 µm/s.

During this measurement, obvious surface defects were avoided to avoid interferences with the data. We ascribe these defects to the lack of real surface treatment/primer and the likely presence of sandblasting residues on the substrate.

Taber abrasion

The Taber abrasion testing was performed according to the ASTM D4060 – 19, using CS-10 grits. The reported weight losses were measured after 1,000 cycles. To improve the adhesion of the coatings, the steel substrate (A1008) was sandblasted on both sides using 100 µm aluminum particles and then thoroughly rinsed under tap water and immediately blew with nitrogen to dry the substrate and remove any residues of sandblasting.

Results

Surface topography of the coatings evaluated in this study:

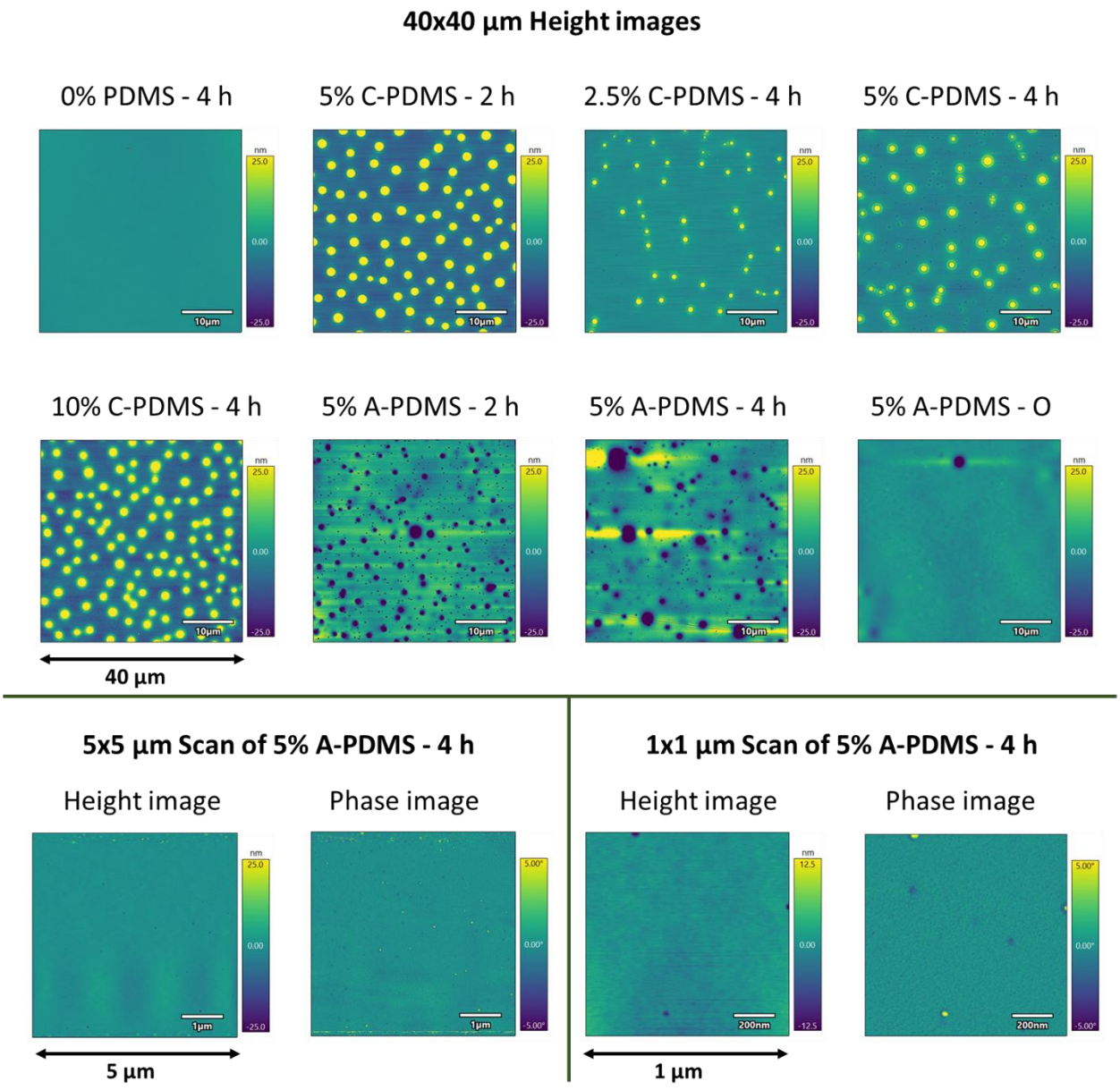

Figure S1: AFM height imaging of the coating surfaces investigated in this study, and smaller size scans performed on 5% A-PDMS - 4 h to further highlight the presence of nanodomains (about 25 nm in diameter) on the surface.

Table S3: Roughness data obtained from AFM height imaging

Sample	% PDMS	Mixing time (h)	Roughness Sq (nm)	Roughness Sa (nm)
PU control	0	4	0.5	0.4

C-PDMS	2.5	4	4.0	1.8
	5	2	19.9	11.9
	5	4	9.6	5.2
	10	4	13.3	9.8
A-PDMS	5	2	13.8	7.1
	5	4	18.7	7.9
	5	Overnight	3.0	1.4

Observation of domains within the bulk of 5% A-PDMS - O through optical microscopy:

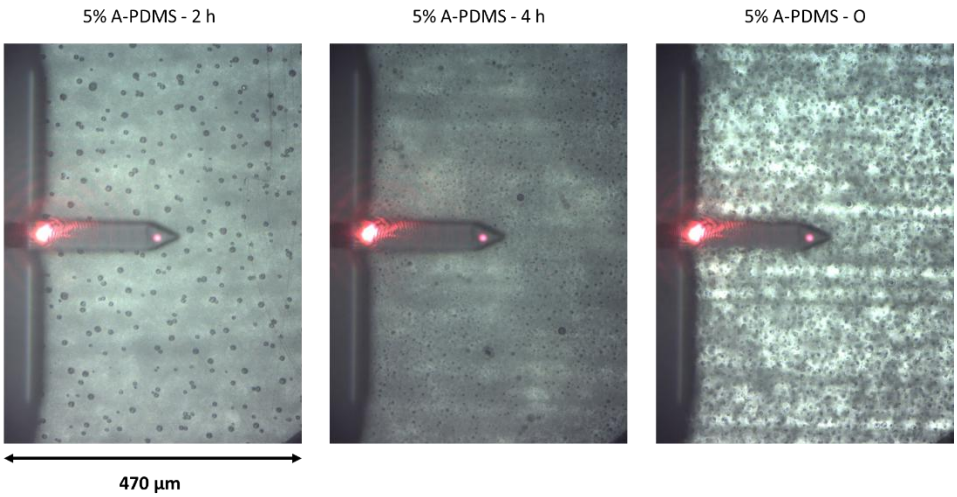

Figure S2: Microscopy images taken during AFM experiment. Domains are visible on the surface for both 2 and 4h of mixing, but for 5% A-PDMS - O, domains were visible only when focusing within the bulk of the material (highlighted by the haziness of the domains [superimposing on multiple depts], the haziness of the probe [focus not on the surface], and the visibility of the substrate streaks)

Determination of the presence of domains within the bulk of the coatings:

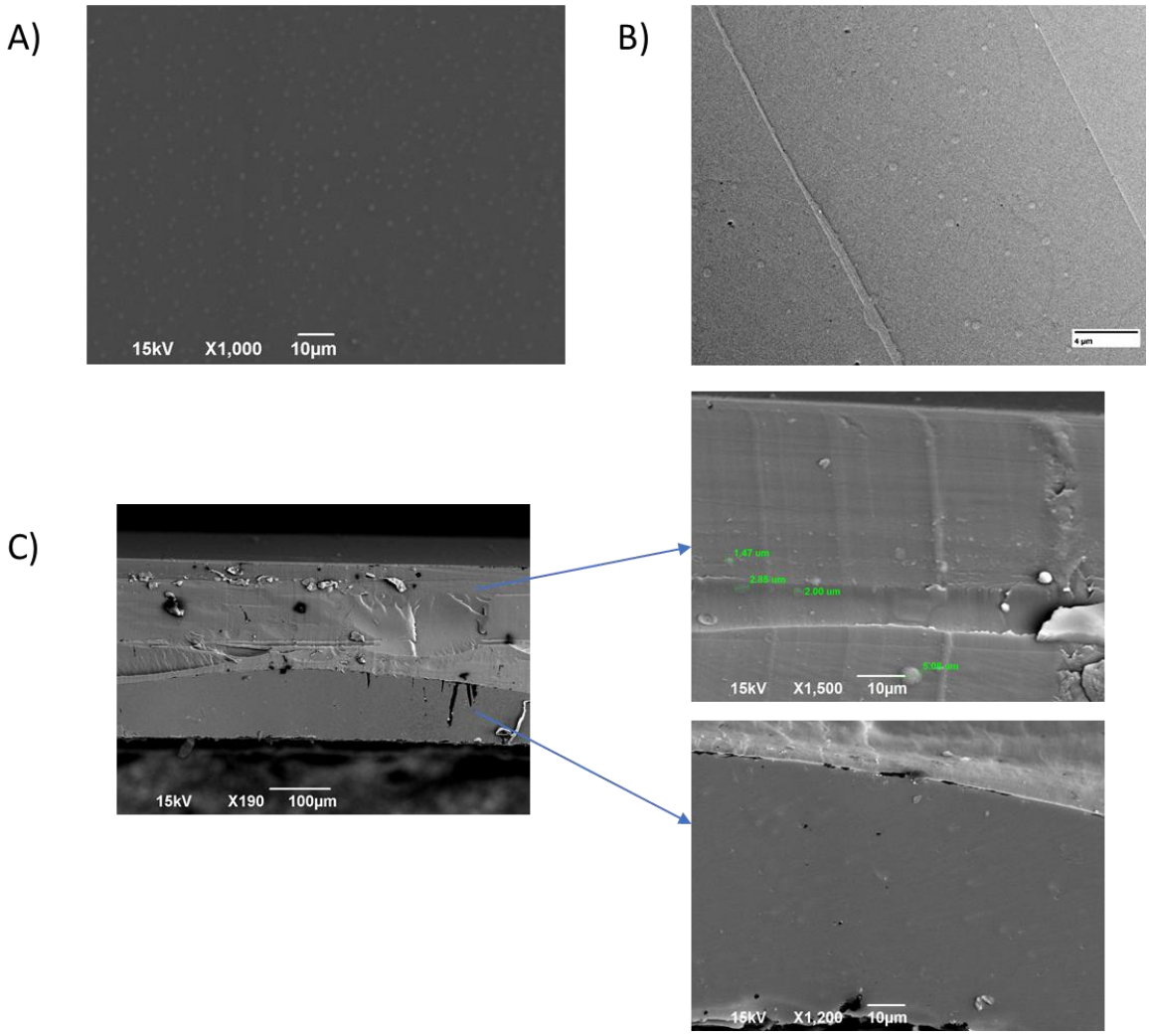

Figure S3: A) SEM imaging of the surface, B) TEM imaging of the cross-section cut (in thickness), and C) SEM imaging of the cross-section cut (in thickness) of a coating containing 5% of PDMS, and mixed 4 hours before application.

Determination of the PDMS nature of the domains:

The Pi-FM analysis was performed using a wavelength of 1085 cm^{-1}, roughly corresponding to the middle of the band of absorption of Si-O-Si bonds,[1] which revealed strong intensity signals inside the round domains observed at the surface (Figure S4.A.). Additionally, spectra recorded when aiming inside the domains with the same apparatus showed significantly more intense signals corresponding to PDMS than the spectra obtained when aiming outside the domains (Figure S4.B.).

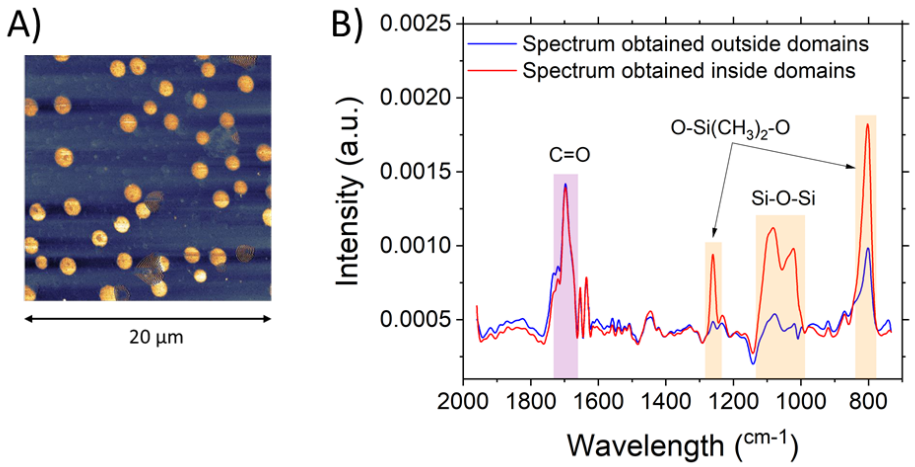

Figure S4: A) Pi-FM analysis of sample 5% C-PDMS - 4h (the laser wavelength used for this experiment is of 1085 cm^{-1} and yellow coloring indicates a high intensity of signal while blue indicates a low intensity). B) Spectra obtained during Pi-FM experiment inside and outside of the domains highlighted on Figure 4.A.

Highlighting the superimposition of C-PDMS ice release data points:

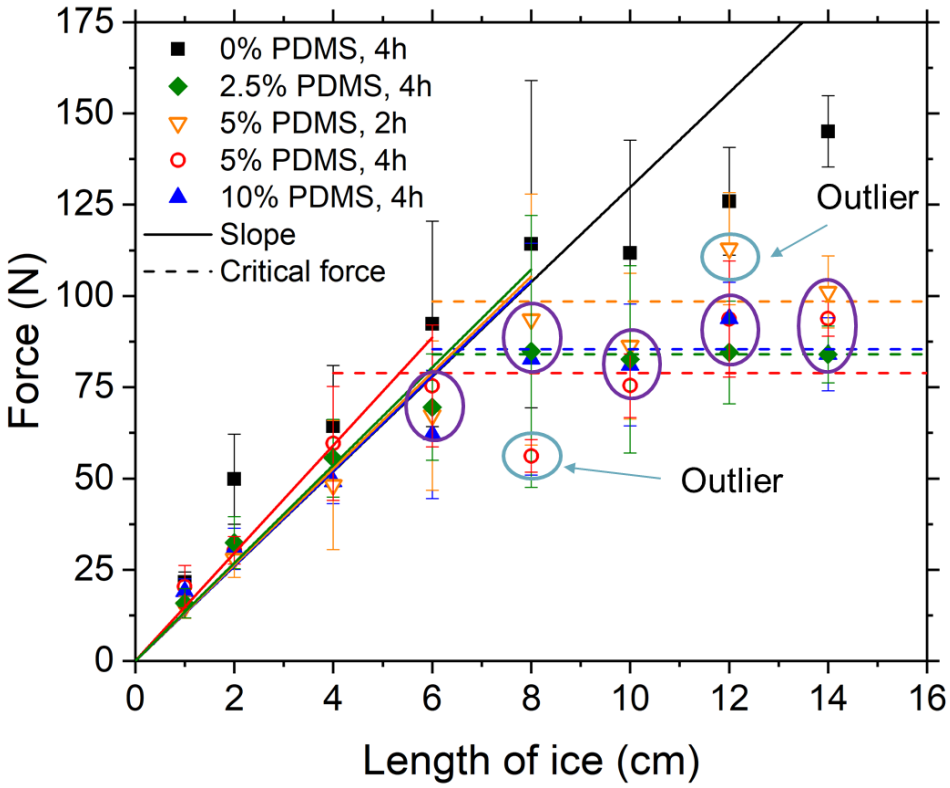

Figure S5: Compilation of forces recorded for the removal of ice samples from the surfaces of C-PDMS samples.

Determination of the presence of PDMS at the interface coating/substrate

Since we demonstrated that PDMS domains were distributed all through the bulk of the coating, and PDMS or other low surface energy coatings are known to present adhesion issues to substrates, we attempted to investigate the presence or absence of PDMS at the interface coating/substrate. For this, 5% C-PDMS - 4h was applied on bare aluminum, peeled off, and the coating interface with the substrate (backside) was investigated by AFM and contact angle measurements (Figure 9). Although the presence of domains was obvious by AFM on the surface of the coating, no domains were visible on the backside. Additionally, in opposition to the surface energy of 22.5 mN/m measured at the surface of the coating, the backside of the coating displayed a surface energy of 41.3 mN/m, corresponding to the one of the PU control (0% PDMS). This observation may be explained by a preferential wetting of the substrate by the PU phase compared to the PDMS phase, which find it source in the PU phase having a higher surface energy than the PDMS and thus preferentially wetting the substrate. These finding suggests the coatings of this study are unlikely to be subject to the traditional adhesion issues encountered with PDMS materials, which was confirmed by crosshatch adhesion testing.

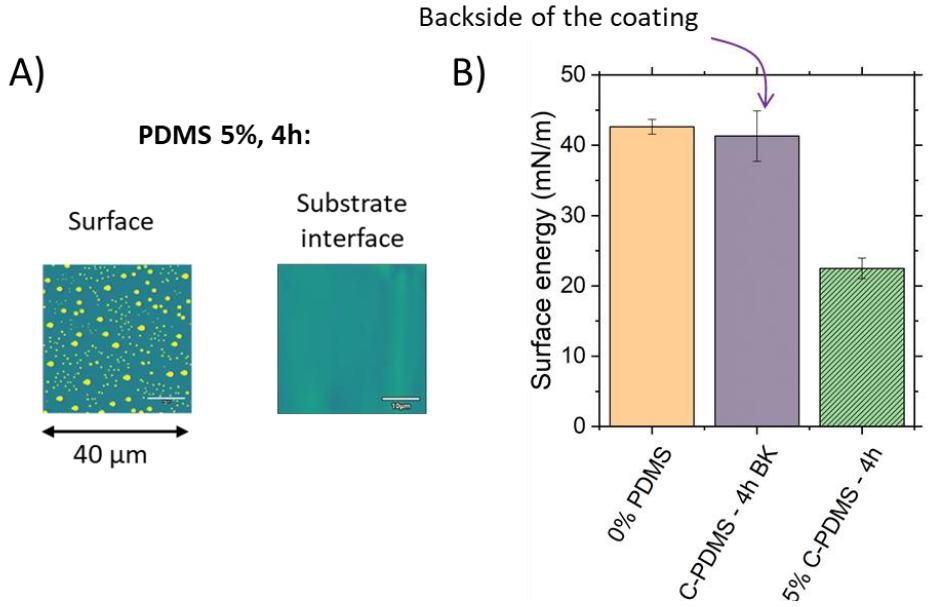

Figure S6: A) AFM imaging of the surface and substrate interface of a coating containing 5% of PDMS, and mixed 4 hours before application. B) Surface energies determined from water and diiodomethane contact angles.

References

[1] B.C. Arkles, W.R. Peterson, R. Anderson, eds., Silicon Compounds Registrer and Review, 3rd editio, Petrarch Systems, 1984.