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Supplementary Information

Durable Gels with Ultra-low Adhesion to Ice

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Section 1. Experimental details.

Fabrication of PDMS gels: We fabricated our polydimethylsiloxane (PDMS) gels by vigorously mixing vinyl-terminated PDMS (v-PDMS, M_n = 95 kDa) and hydride-terminated PDMS (h-PDMS, M_n = 1.3 kDa) in a stoichiometric ratio of 10:1 along with the desired amount of non-reactive trimethyl-terminated PDMS (t-PDMS, molecular weight M_n = 2 kDa or 28 kDa). The mixture of v-PDMS, h-PDMS and t-PDMS was degassed in a vacuum oven and spin coated on a glass microscope slide. The desired coating thickness was obtained by adjusting the spin coating speed. The spin coated mixture was subsequently cross-linked in an oven at 70°C for 24 hours, resulting in the desired PDMS gel.

Fabrication of lubricated surfaces: We fabricated lubricated surfaces by directly spin coating Krytox$^{\text{TM}}$ 104 on a microscope glass slide at a speed of 500 rpm for 2 minutes.

Measurement of thickness and roughness: The thickness and root mean square (RMS) roughness of all of our PDMS gels were measured using an optical profilometer (Zygo Zescope). The RMS roughness of all of our as fabricated PDMS gels is 0.05 μm ± 0.01 μm, indicating that the surfaces of our as fabricated PDMS gels are smooth (i.e., non-textured).

Measurement of shear modulus: Dynamic rheological measurements were performed at -20°C (in a controlled temperature chamber) using a rheometer (TA Instruments, ARES-G2) with 8 mm parallel plate geometry to determine the shear modulus μ of our PDMS gels. The temperature of -20°C was chosen to match the temperature of the ice adhesion strength measurements. Strain sweeps were first performed to determine the linear viscoelastic regime of our PDMS gels. Subsequently, frequency sweeps were conducted within the linear viscoelastic regime to measure the storage modulus μ' and the loss modulus μ'' in the plateau region (typically 10 rad s^{-1} to 100 rad s^{-1} in our experiments). For all of our PDMS gels, the storage modulus μ' in the plateau region was about an order of magnitude higher than the loss modulus μ'', i.e., $\mu' >> \mu''$. Then, we determined the shear modulus, $\mu = \sqrt{\mu'^2 + \mu''^2} \approx \mu'$, i.e., the shear modulus is determined by measuring the plateau modulus.

Measurement of ice adhesion strength: The ice adhesion strength of PDMS gels was measured using a custom-built apparatus. Our apparatus includes a Peltier plate with a temperature controller, a force gage equipped with a probe and connected to a data acquisition system, and a linear transition stage on which the force gage is mounted (see SI, section 5). In a typical ice adhesion strength measurement, the PDMS gel was placed on the Peltier plate and 500 μ of water in a cuvette was placed in direct contact with the surface of coating. The Peltier plate was maintained at a temperature of -20°C for 1 hour. During this time, water in the cuvette froze to form ice that adhered to the PDMS gel. Subsequently, the linear translation stage was moved at a shear rate $\dot{\gamma}$ = 0.8 mm s^{-1} (similar to prior work[1, 2]) such that the probe applied a shear force (i.e., tangential to the surface of the coating) on the entire width of the cuvette until ice was detached from the surface of PDMS gel. The distance between the plane of shear force and the PDMS gel surface was < 1 mm to mimic pure shear to the extent possible experimentally. The shear force applied by the probe was measured continuously with the force gage and the data acquisition system. Our experiments indicated that the adhesion between the cuvette and the coated surface is negligible compared to the adhesion between ice and the coated surface.

Assessment of mechanical durability via abrasion tests: A Taber linear abraser (Taber Industries, Model 5750) was used to conduct abrasion tests on our PDMS gels. The abrasion tests were performed at 25 cycles min^{-1} with 400-grit sandpaper under a pressure of 6.8 kPa and a stroke length of 2.54 cm. During repeated icing/deicing cycles and abrasion tests with a sandpaper, we did not observe adhesive failure at the interface of PDMS gels and the glass microscope slide. However, the adhesion between our PDMS gels and the underlying substrates can perhaps be improved by introducing an adhesive layer.

Section 2. Work of adhesion between ice and an adhering solid.

From a thermodynamic perspective, the work of adhesion W_{adh} between ice and a solid material is given as,

$$W_{adh} = \gamma_{ia} + \gamma_{sa} - \gamma_{si} \tag{S1}$$

Here, γ_{ia} is ice surface energy (i.e., ice-air interfacial energy), γ_{sa} is the solid surface energy (i.e., solid-air interfacial energy) and γ_{si} is the solid-ice interfacial energy (Figure S1a). Recognizing that the ice surface energy (γ_{ia} = 75 mJ m^{-2})[1, 3, 4] is approximately equal to the water surface energy (or surface tension, γ_{wa} = 72 mJ m^{-2}) and assuming that the ice-surface interfacial energy γ_{si} is approximately equal to the water-surface interfacial energy γ_{sw},[1, 3, 4] one can rewrite the work of adhesion as,

$$W_{adh} = \gamma_{wa} + \gamma_{sa} - \gamma_{sw} \tag{S2}$$

The hydrophobicity or hydrophilicity of a non-textured solid material is given by the Young's equation as,[5]

$$\gamma_{wa} \cos\theta_Y = \gamma_{sa} - \gamma_{sw} \tag{S3}$$

Here, θ_Y is the Young's contact angle of water on the solid surface. Combing Equations (S2) and (S3), we obtain,

$$W_{adh} \approx \gamma_{wa}\left(1 + \cos\theta_Y\right) \tag{S4}$$

From this equation, it is evident that hydrophobic materials with $\theta_Y > 90^\circ$ display lower adhesion to ice compared to hydrophilic materials with $\theta_Y < 90^\circ$. Thus, it is not surprising that over the past few decades, many researchers have conducted experiments and reported lower τ_{ice} with hydrophobic materials compared to hydrophilic materials.[1, 6-8] In this work, one of the reasons for our choice of PDMS is its hydrophobicity.

We measured the advancing and receding contact angles of water on our PDMS gels fabricated with different t-PDMS concentrations and molecular weights (Figure S1b). It is evident that the contact angles are independent of the t-PDMS concentrations and molecular weights. Based on Equation (S4), these results imply that the work of adhesion between ice and our PDMS gels is not altered by varying the concentration or molecular weight of t-PDMS. Assuming that the Young's contact angle is approximately equal to the advancing contact angle, we estimated the work of adhesion between ice and our PDMS gels $W_{adh} \approx 0.047$ J m^{-2} ± 0.001 J m^{-2}.

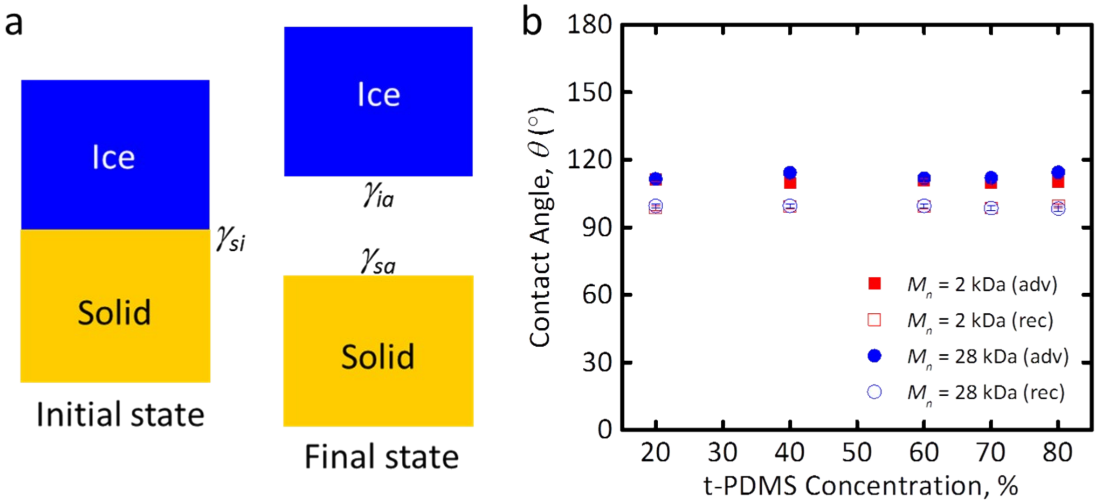

Figure S1. a) Schematic depicting the interfacial energies in the adhesion of ice to a solid. b) The measured advancing and receding contact angles of water on our PDMS gels fabricated with different t-PDMS concentrations and molecular weights.

Section 3. Cohesive failure and adhesive failure between ice and a soft material.

It is evident from Equation 1 in the main manuscript that soft materials with low shear modulus μ are desirable for ultra-low ice adhesion strength τ_{ice}. However, too low of a μ (e.g., liquid lubricants with $\mu \approx 0$) leads to a cohesive failure within the soft materials (i.e., liquid lubricant) during the removal of ice (**Figure S2**). In other words, when ice slides past the lubricated material, the surface of ice shaves off some of the liquid lubricant. Typically, this is evident from the residue of the liquid lubricant on ice upon complete separation. This results in poor mechanical durability due to the sacrificial nature (i.e., loss) of the liquid lubricant. Further, as the liquid layer continues to deplete with the increasing icing/deicing cycles, we anticipate that the ice adhesion strength will eventually increase (see Figure 3c in the main manuscript). In contrast, there is no residue of our PDMS gels on ice or vice versa (evident from visual inspection and touch, ice adhesion strength scaling as the square root of the ratio of shear modulus and thickness as shown in Figure 2c in the main manuscript, stick-slip behavior and separation pulses evident from the force-displacement curves shown in Figure 3a in the manuscript and Movie S1, and virtually unlimited icing/deicing cycles with constant ultra-low ice adhesion strength as shown in Figure 3c in the main manuscript) upon complete separation between ice and PDMS gel. This is indicative of an adhesive failure (without loss of material). Consequently, our PDMS gels maintain their mechanical durability, as evidenced by the unaltered ultra-low $\tau_{ice} \approx 5$ kPa even after 100 icing/deicing cycles (see Figure 3c in the main manuscript).

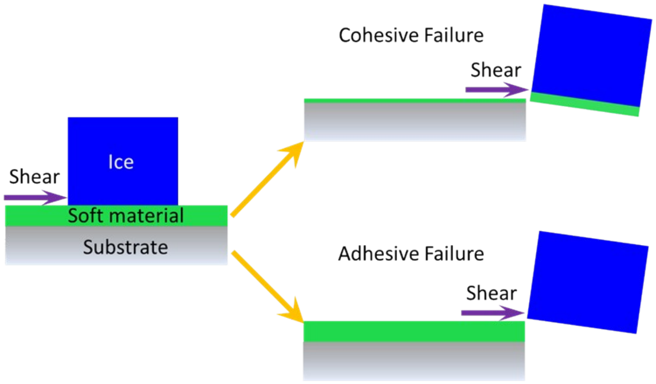

Figure S2. Schematic showing the cohesive failure (i.e., within the material) and adhesive failure (i.e., at the interface of ice and material) during the separation of ice from a soft material.

Section 4. Dynamic rheological measurements

Dynamic rheological measurements were performed at -20°C (in a controlled temperature chamber) using a rheometer (TA Instruments, ARES-G2) with 8 mm parallel plate geometry to determine the shear modulus μ of our PDMS gels. The temperature of -20°C was chosen to match the temperature of the ice adhesion strength measurements. Strain sweeps were first performed to determine the linear viscoelastic regime of our PDMS gels. Subsequently, frequency sweeps were conducted within the linear viscoelastic regime to measure the storage modulus μ' and the loss modulus μ'' in the plateau region (typically 10 rad s^{-1} to 100 rad s^{-1} in our experiments).[9] For all of our PDMS gels, the storage modulus in the plateau region was about an order of magnitude higher than the loss modulus, i.e., $\mu' >> \mu''$ (see Figures S3a and S3b). Then, we determined the shear modulus, $\mu = \sqrt{\mu'^2 + \mu''^2} \approx \mu'$, i.e., the shear modulus is determined by measuring the plateau modulus.

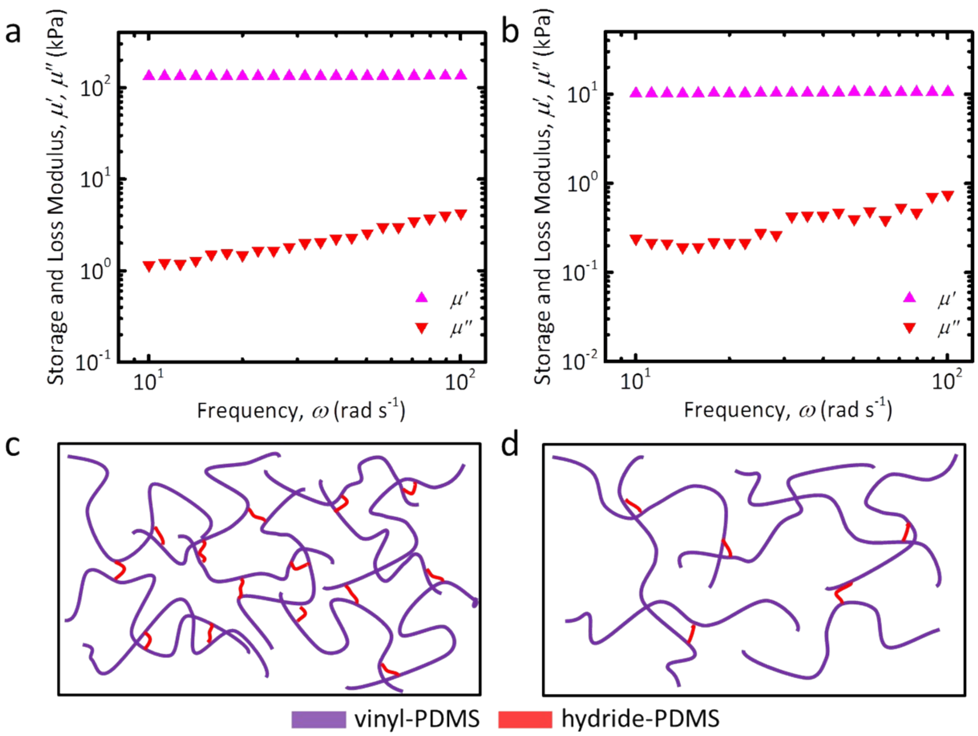

Figure S3. Representative frequency sweeps for the storage modulus μ' and loss modulus μ'' of our PDMS gels fabricated with t-PDMS molecular weight M_n = 2 kDa at concentrations of a) 20%, and b) 80%. c) and d) Schematics depicting the network structures of PDMS gels fabricated at low (e.g., 20%) and high (e.g., 80%) t-PDMS concentrations, respectively.

As shown in Figures S3a and S3b as well as Figure 1b, the shear modulus of our PDMS gels decreased with increasing concentration of t-PDMS in the hydrosilylation mixture. This is because t-PDMS (a non-reactive oligomer) serves as a plasticizer by impeding the cross-linking.[10, 11] With increasing t-PDMS concentration, the cross-link density of the PDMS network decreases (see Figures S3c and S3d), leading to the PDMS gels with lower shear modulus. Our observations (i.e., visual inspection and touch, ice adhesion strength scaling as the square root of the ratio of shear modulus and thickness as shown in Figure 2c in the main manuscript, stick-slip behavior and separation pulses evident from the force-displacement curves shown in Figure 3a in the manuscript and Movie S1, and virtually unlimited icing/deicing cycles with constant ultra-low ice adhesion strength as shown in Figure 3c in the main manuscript) indicate that our fabrication technique results in a PDMS gel without a free liquid layer of trimethyl terminated PDMS on the surface.

Section 5. Experimental apparatus for measuring ice adhesion strength

Our custom-built apparatus for measuring the ice adhesion strength of our PDMS gels includes a Peltier plate with a temperature controller, a force gage equipped with a probe and connected to a data acquisition system, and a linear translation stage on which the force gage is mounted (Figures S4a and S4b). In a typical τ_{ice} measurement, the surface spin coated with desired PDMS gel was placed on the Peltier plate and water in a cuvette was placed in direct contact with the PDMS gel. The Peltier plate was maintained at a temperature of -20°C for 1 hour. During this time, water in the cuvette froze to form ice that adhered to the PDMS gel. Then the linear translation stage was moved at a shear rate $\dot{\gamma}$ = 0.8 mm s^{-1} such that the probe applied a shear force (i.e., tangential to the PDMS gel surface) on the entire width of the cuvette until ice detached from the PDMS gel. The force was applied as close as possible to the bottom of the cuvette to mimic pure shear loading. The shear force applied by the probe was measured continuously with the force gage and the data acquisition system.

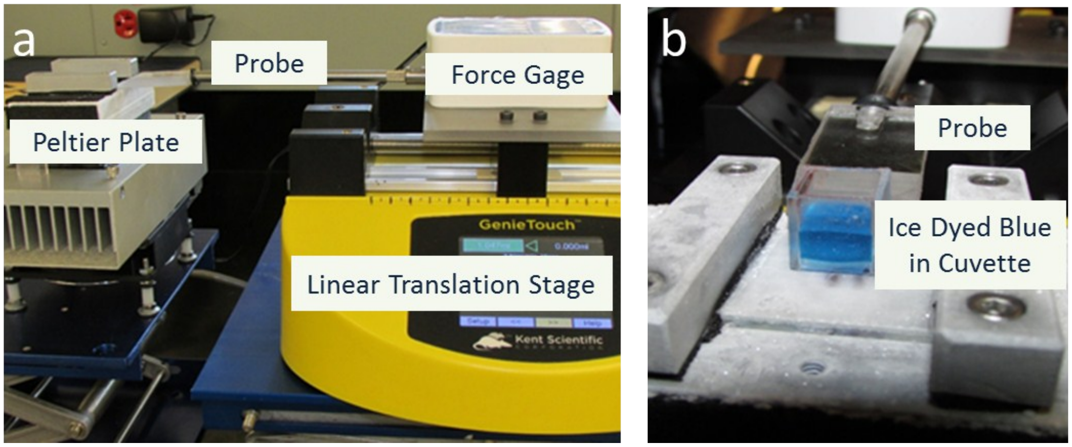

Figure S4. a) Picture of our ice adhesion strength measurement apparatus. b) Picture of ice (dyed blue) in a cuvette on the Peltier plate.

Section 6. Influence of freezing time and water volume on ice adhesion strength

In order to evaluate the influence of freezing time on the measured ice adhesion strength, we conducted ice adhesion strength measurements using 500 μl deionized (DI) water, which was subjected to different freezing times to form ice. As the freezing time was varied from 0.5 h to 24 h, there was no significant change in measured ice adhesion strength of our PDMS gels (Figure S5a). We also evaluated the influence of water volume (and correspondingly the normal stress acting downward on the ice-PDMS gel interface) on the measured ice adhesion strength using 24 h freezing time. As the water volume was varied from 250 μl to 1500 μl (the corresponding normal stress varied from approximately 25 Pa to 150 Pa), there was no significant change in the measured ice adhesion strength (Figure S5b). Note that the normal stresses used in prior work,[1, 12-16] lie within the range of our measurements. For the range of normal stresses considered in this work, the separation of ice from our PDMS gels occurred via separation pulses. It is worth noting that increasing the normal stresses (or water volume) significantly could potentially result in the transition of the separation mechanism from separation pulses to slip pulses.[17]

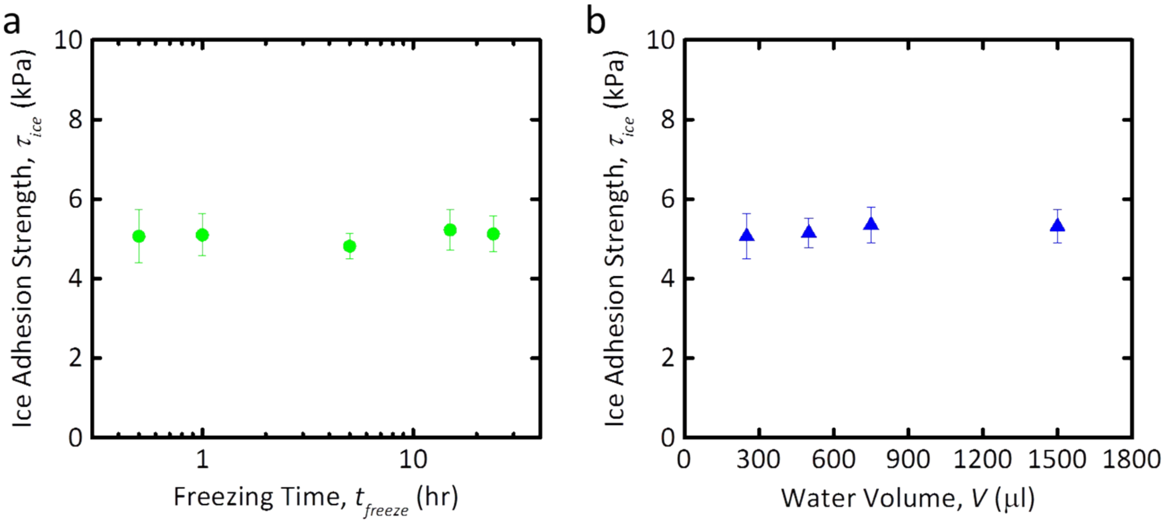

Figure S5. a) The ice adhesion strength of our PDMS gels does not change significantly with changing freezing time. b) The ice adhesion strength of our PDMS gels does not change significantly with changing water volume (or ice block height). The PDMS gel used for these experiments was fabricated using t-PDMS molecular weight M_n = 2 kDa and concentration of 80%. Similar behavior was observed with other PDMS gels as well.

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Movie Legends

Movie S1. This video illustrates the separation of ice from our PDMS gels under a shear force. A close examination of the interface between ice and PDMS gel during sliding indicates that separation pulses propagate along the direction of the motion of the rigid body (i.e., ice).