

Grafting Silicone at Room Temperature—a Transparent, Scratch-resistant Nonstick Molecular Coating

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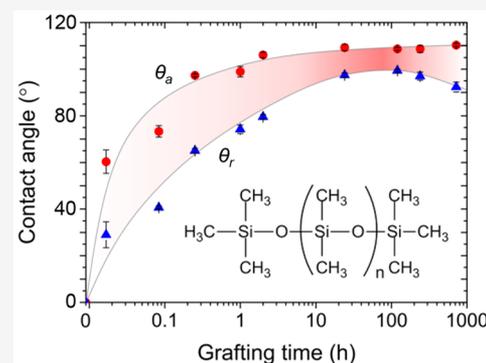


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Supporting Information

ABSTRACT: Silicones are usually considered to be inert and, thus, not reactive with surfaces. Here we show that the most common silicone, methyl-terminated polydimethylsiloxane, spontaneously and stably bonds on glass—and any other material with silicon oxide surface chemistry—even at room temperature. As a result, a 2–5 nm thick and transparent coating, which shows extraordinary nonstick properties toward polar and nonpolar liquids, ice, and even super glue, is formed. Ten microliter drops of various liquids slide off a coated glass when the sample is inclined by less than 10°. Ice adhesion strength on a coated glass is only 2.7 ± 0.6 kPa, that is, more than 98% less than ice adhesion on an uncoated glass. The mechanically stable coating can be easily applied by painting, spraying, or roll-coating. Notably, the reaction does not require any excess energy or solvents, nor does it induce hazardous byproducts, which makes it an ideal option for environmentally sustainable surface modification in a myriad of technological applications.



INTRODUCTION

Silicones are colorless, nontoxic, and generally considered to be biocompatible materials. Silicones are frequently used in industry and a broad range of consumer products worldwide.^{1–3} The global market for silicones is rapidly increasing and is expected to reach 20 billion U.S. dollars in 2021.⁴ The unique properties of silicones include excellent thermal stability, thermal and electrical insulation, and water repellency. Important fields of applications of silicones cover medical technology, construction, automotive, and paper industry. Typical examples are top coatings for medical devices, electronics, solar cells, optical lenses, window panes, release layers for adhesive labels, containers, and food packages.^{1,2,5} The unique properties of silicones result from the inorganic–organic composite structure of siloxane molecules.

The most common silicone is trimethylsiloxy terminated linear poly(dimethylsiloxane) (PDMS). It has an inorganic silicon (Si)–oxygen (O) backbone with two organic methyl side groups ($-\text{CH}_3$) attached to each silicon atom (Supporting Information, Figure S1).¹ The organic/inorganic molecular structure gives PDMS its unique properties. For example, the low electronegativity of Si leads to highly polarized Si–O bonds in PDMS backbone (Supporting Information, Table S1). The large bond energy of 452 kJ mol^{-1} gives PDMS its high thermal stability.¹ The hydrophobic methyl side groups provide low surface energy and shield the inorganic Si–O backbone, thereby lowering intermolecular interactions within PDMS. Because of its low surface tension $\gamma \approx 20 \text{ mN m}^{-1}$ PDMS easily wets most materials.¹ The wide bond angle of

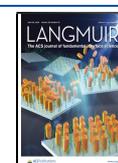
$\sim 150^\circ$ between Si–O–Si atoms yield nearly vanishing torsional barriers.⁶ As an instructive example, the rotation energy around a $(\text{CH}_3)_2\text{Si}-\text{O}$ bond in PDMS is only 3.3 kJ mol^{-1} , whereas around a CH_2-CH_2 bond in polyethylene it is 13.8 kJ mol^{-1} .¹ The low glass transition temperature T_g at -127°C ¹ ensures excellent lubricating properties over a wide range of temperatures.

It is common knowledge that silicones tend to stick to surfaces. It has been shown that treating PDMS on oxide surfaces by heat^{7,8} yields strongly bound, polymer brush^{9,10}-like PDMS films. Such films show remarkable liquid-repellency and exhibit a low contact angle hysteresis less than or equal to 10° for various polar and nonpolar liquids. In comparison, other hydrophobic coatings like fluorosilanes¹¹ and Teflon¹² (poly(tetrafluoroethylene), PTFE) typically show water contact angle hysteresis of $\sim 20\text{--}30^\circ$. In addition to being bound to surfaces by the use of heat, PDMS can be bound on metal oxide photocatalysts by illumination with UV light.¹³ For example, Eifert et al.¹⁴ applied PDMS on various substrates, including glass, and baked the samples for 1–3 min at 300°C to attach PDMS to the surfaces. Thereafter they impregnated the samples with PDMS to achieve liquid-repelling oil-infused

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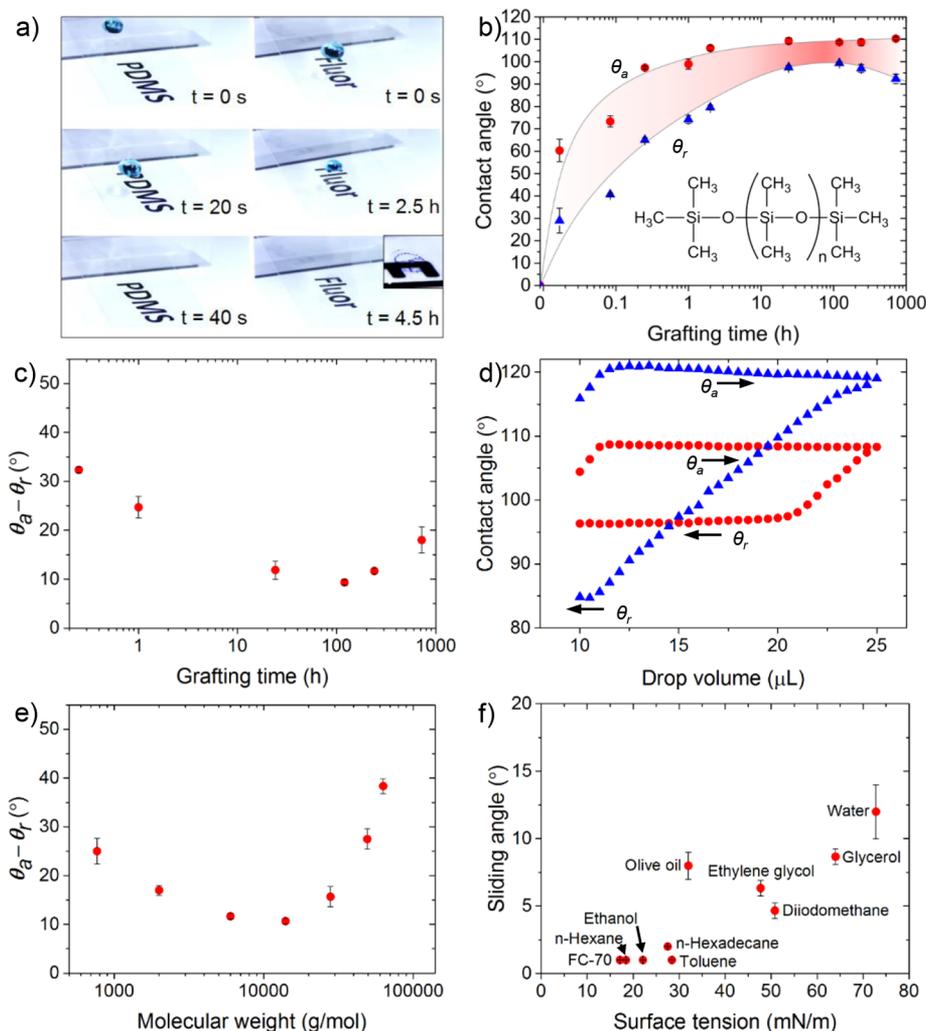


Figure 1. PDMS films grafted to glass at room temperature. (a) (left) Photographs showing a methylene blue dyed water drop (radius ≈ 2 mm) sliding down on the PDMS film. The drop leaves behind a clean surface. The molecular weight of PDMS was 6000 g mol^{-1} and grafting time was 24 h. (right) The drop is pinned to a chemical vapor deposited fluorosilane coating on glass. The drop evaporates and leaves behind a stain (inset). Both surfaces were inclined by 15° . (b) Advancing θ_a (red dots) and receding θ_r (blue triangles) water contact angles (inset: molecular formula of PDMS) and (c) contact angle hysteresis on the PDMS films after different grafting periods. (d) Contact angle vs volume of water drop on the grafted PDMS (red dots) and cross-linked PDMS (blue triangles) on glass when inflating and deflating the drop. Advancing and receding contact angles are consistently defined throughout the work by increase and decrease of the drop volume between 10 and $25 \mu\text{L}$ at a constant rate of $1 \mu\text{L s}^{-1}$ using a standard contact angle goniometer. (e) Contact angle hysteresis of water on films grafted with different molecular weights of PDMS. (f) Sliding angles for $10 \mu\text{L}$ drops of different polar and nonpolar liquids on the PDMS film. Surface tensions γ of the liquids are Fluorinert FC-70 17.1 mN m^{-1} ; *n*-hexane 18.4 mN m^{-1} ; ethanol 22.1 mN m^{-1} ; *n*-hexadecane 27.5 mN m^{-1} ; toluene 28.4 mN m^{-1} ; olive oil 32 mN m^{-1} ; ethylene glycol 47.7 mN m^{-1} ; diiodomethane 50.8 mN m^{-1} ; glycerol 64 mN m^{-1} ; water 72.8 mN m^{-1} . In (a–d) and (f) PDMS molecular weight was 6000 g mol^{-1} . In (a) and (d–f) grafting time was 24 h.

surfaces. Xue et al.¹⁵ fabricated a superhydrophobic PDMS/octadecylamine coating on fabrics that showed self-healing ability after both mechanical and chemical damage. Yang et al.¹⁶ applied drop coating, curing, and abrasion to fabricate a superhydrophobic ZnO/PDMS coating with ice-repelling properties. Besides coating applications, interactions between PDMS and solids¹⁷ are of fundamental and practical importance, for instance, in binding inorganic filler particles used to reinforce silicone rubber.¹⁸ Other sophisticated applications based on organosilica architecture include environmental sensors¹⁹ and filtration of nanoparticles.²⁰

Despite the abundant use of PDMS, its reactions with oxides are not clear. The first paper pointing out the heat-activated reaction of PDMS with glass was published already in 1947 by Hunter et al.²¹ In 1969, Willis²² wrote: “We have observed

greatly enhanced reaction at metal surfaces. Decomposition of the polydimethylsiloxanes can occur at temperatures as low as $90\text{--}100^\circ\text{C}$, resulting in the formation of extremely thin polymeric films.” He pointed out that the reaction only occurs on metal oxide surfaces, not on noble metals, and that the reaction was not observed under inert gas atmospheres of nitrogen and argon. These early works, however, did not get wide attention, because PDMS was considered to be unreactive on oxides, that is, not capable of forming any covalent bonds with the substrate, as it does not contain any reactive groups such as chlorine ($-\text{Cl}$) or hydroxyl ($-\text{OH}$) groups. Adsorption of PDMS was explained by hydrogen bonding with the substrate.²³ The possibility of a chemical surface reaction was not considered until 2010, when Krumpfer and McCarthy^{7,8} and, four years later, Graffius et

al.²⁴ proposed that PDMS can adsorb to silicon oxide via acid-catalyzed surface reaction, which involves scission of the siloxane backbone of PDMS and condensation with the surface silanols ($\equiv\text{Si}-\text{OH}$) at elevated temperatures at 100–300 °C.

It has been proposed that surface silanols are favorable sites for chemical bonding of PDMS on silicon oxide.^{7,8,24} Fully hydroxylated silicon dioxide surface has a considerable amount of surface silanols, $\sim 5 \text{ OH nm}^{-2}$.^{24–26} Despite these silanol groups, spontaneous formation of a high-quality coating film from PDMS without adding reagents or catalysts seems surprising at first sight, as PDMS does not contain any reactive groups. The reaction is of particular industrial interest, because producing molecular PDMS coatings typically releases toxic chemicals^{1,27} or consumes energy.^{8,14} On thicker cross-linked PDMS coatings liquid drops pin to the surface. This problem has been overcome by infiltrating PDMS with silicone oil, giving rise to lubricant-infused surfaces.^{14,28–30} The drawback of such an approach is that the sliding drops take the lubricant along, ruining the properties in the course of time (Supporting Information, Video S1).^{31,32}

Here we overcome the problems related to production of PDMS surfaces and the adhesion of drops by introducing an easy, but unexplored, strategy. We show that PDMS spontaneously reacts with silicon oxide surfaces over a wide range of temperatures, even at room temperature and below. We propose that the grafting reaction of PDMS to silicon oxide at room temperature is induced by attachment of linear PDMS chains to the surface via hydrolysis and condensation reactions. Notably, the reaction yields a 2–5 nm thick, high-quality coating, which shows contact angle hysteresis below 10° for water and a variety of organic liquids on both glass and silicon wafers (Figure 1). The PDMS film thus enables easy sliding of various polar and nonpolar liquids on its surface. Gravity or a gentle blow easily removes the drops, thus helping the surface to stay clean (Figure 1a and Supporting Information, Video S2). Notably, this environmentally friendly, one-step synthesis yields a liquid-repellent, transparent, mechanically stable, and nonstick coating that is capable of repelling ice, spray paints, and adhesives, including super glue. Solid and porous surfaces of any shape can easily be coated including paper and textiles (Supporting Information, Video S3).

MATERIALS AND METHODS

Materials. The substrate materials were 170 μm thick borosilicate cover glass slides (Menzel-Gläser, Thermo Scientific) and mirror-polished silicon wafers (Si-Mat). Additionally, 1 mm thick soda-lime laboratory glass (Menzel-Gläser, Thermo Scientific) was used as a substrate for demonstrating the stability and easy-to-clean properties of the coating. Linear PDMS with molecular weights (MW) of 770 and 49 350 g mol^{-1} was purchased from Gelest, Inc., and PDMS of MW 2000, 6000, 14 000, 28 000, 63 000, and 117 000 g mol^{-1} were from Alfa Aesar. The cyclic PDMS, dodecamethylcyclotetrasiloxane (D5), MW 371 g mol^{-1} , was purchased from Sigma-Aldrich. Milli-Q water was used for the experiments. All technical probe liquids were purchased from Sigma-Aldrich and used as received.

Sample Preparation. The glass and silicon wafer substrates were washed with ethanol and water, dried under nitrogen flow, and if not otherwise stated, oxygen-plasma cleaned at 300 W for 10 min (Femto low-pressure plasma system, Diener electronic). A few drops of PDMS (i.e., a silicone oil with a defined molecular weight), ~ 30 – $50 \mu\text{L}$ in total, were dropped on the substrate surface, after which the drops were spread with another glass slide to form a less than 1 mm thick PDMS film. We used PDMS with a molecular weight of 6000 g mol^{-1} (viscosity = 95 mPa s) in all the experiments, if not otherwise stated. After the PDMS films were spread on the substrates, the

samples were placed in plastic polystyrene containers at a temperature of 22–23 °C and relative humidity of 30–60% for 24 h to let it react with the sample surface, if not otherwise stated. The containers were not sealed gas proof. Some samples were grafted at varying temperatures. Therefore, the PDMS films were spread on the samples as described above, after which the samples were placed in an oven, fridge, or freezer for 24 h. The PDMS grafting at varying humidity at room temperature was performed in a custom-made chamber, where the relative humidity (RH) was controlled by circulating dry or moist nitrogen gas. After PDMS reacted with the glass (or silicon wafer) surface, the excess PDMS was washed away first by a rinse with toluene and then by sonication of the sample in toluene, ethanol, and water for 10 min in each liquid.

Surface methylation and fluorosilanization were performed by applying chemical vapor deposition (CVD). The plasma-cleaned glass substrates were placed in a desiccator together with 100 μL of the silane, trimethylchlorosilane, or 1H,1H,2H,2H-perfluorooctyl-trichlorosilane (97% pure, Sigma-Aldrich). The pressure in the desiccator was reduced to ~ 100 – 200 mbar for 2 h. Thereafter, the samples were placed in a vacuum oven at 60 °C for 2 h to remove any unreacted silane. To compare the grafted PDMS films with a cross-linked PDMS, we prepared cross-linked PDMS surfaces using Sylgard 184 elastomer (Dow Corning). The base component and the cross-linker were mixed at a ratio of 10:1 in weight by manually stirring for 2 min. The solution was degassed in vacuum at 200 mbar for 15 min. After that, $\sim 30 \mu\text{L}$ of the PDMS solution was deposited on glass substrates of 24 mm \times 30 mm in size. The samples were spin-coated at 2500 rpm for 5 min to form an $\sim 10 \mu\text{m}$ thick PDMS film, after which the surfaces were cured in an oven at 60 °C for 20 h. To compare with a lubricant-infused surface, we infused the cross-linked PDMS film with a PDMS fluid (MW 6000 g mol^{-1}). Therefore, we deposited a few drops of the PDMS on the sample and let them spontaneously spread over the surface. After the film was allowed to impregnate for 2 h in a horizontal plane, the sample was placed vertically for 5 h so that excess PDMS was removed from the surface by gravity. The surface showed a sliding angle of less than 1° for 10 μL water drops.

To demonstrate PDMS grafting to other materials, which do not have silicon oxide surface chemistry, we coated aluminum, stainless steel, polyester fabric, and paper with PDMS. The metal plates, 50 mm \times 50 mm \times 1 mm in size, were purchased from Modulor and were washed with ethanol and water prior to use. The fabrics were purchased from Karstadt, and the paper tissues (Kimtech Professional precision wipes, Kimberly-Clark) were from Thermo Fisher Scientific. Prior to applying the PDMS films, we coated the substrates with a thin, $\sim 3 \text{ nm}$ thick silicon dioxide layer. Therefore, the substrates were first oxygen-plasma cleaned (aluminum and stainless steel at 300 W for 10 min and polyester fabric and paper at 180 W for 2 min). Thereafter, the substrates were placed in a desiccator together with ammonia (3 mL, 25% solution, VWR Chemicals) and TEOS (3 mL, 98% pure, Sigma-Aldrich) at atmospheric pressure and room temperature for 4 h to apply a gas-phase Stöber-like reaction³³ to grow the silica layer. Then the samples were oxygen-plasma cleaned again using the same parameters that were used prior to growing the silica shell, after which PDMS was grafted to the samples for 24 h at room temperature. To remove unreacted PDMS, the metal plates were sonicated in the solvents using the standard procedure described above. The polyester fabric and paper samples were simply rinsed for $\sim 30 \text{ s}$ in each solvent (paper was only rinsed in toluene and ethanol, not in water, to prevent damaging the substrate).

Characterization. Contact Angle. Surface wetting was investigated using a DataPhysics OCA 35 goniometer (DataPhysics Instruments). Static contact angles θ and sliding angles α were determined with 10 μL drop volume. The data were collected from at least three different positions on each sample. Advancing θ_a and receding θ_r contact angles were determined by increasing and decreasing the drop volume between 10 and 25 μL at the rate of 1 $\mu\text{L s}^{-1}$.

Ellipsometry. The thickness of the grafted PDMS films was determined by ellipsometry (Nanofilm EP3, 658 nm laser, 50 mW) on silicon wafers. The thickness of the native oxide layer on the wafers

was measured to be 3.8 ± 1.5 nm. The thickness of the native oxide layer enters the calculation of the thickness of the PDMS film. Because the refractive index values of PDMS ($n = 1.42$, $\lambda = 500$ nm)³⁴ and native oxide ($n = 1.46$, $\lambda = 500$ nm)³⁵ are very close, the light is primarily reflected at the interface between the native oxide layer and silicon ($n = 4.3$, $\lambda = 500$ nm).³⁵

AFM. The PDMS film thickness and the adhesion force between the PDMS film surface and the atomic force microscopy (AFM) tip were investigated by AFM (MFP3D Standalone from Asylum Research). Uncoated Si cantilevers (OMCL-AC240 by Olympus) with force constant between 2.6 and 3.1 N m⁻¹ were used. For each substrate, we used a new cantilever that we calibrated by analyzing the thermal noise spectrum ("Sader method"). Force–Distance curves were recorded in a force mapping approach: the tip was repeatedly approached and retracted on a grid of 64 by 64 points (32 by 32 points on the glass reference) on an area of 1 $\mu\text{m} \times 1 \mu\text{m}$. This way, the tip always measured a pristine surface.

XPS. The influence of different grafting times and pretreatment on the atomic composition on the silicon wafers was investigated by X-ray photoelectron spectroscopy (XPS). XPS analyses were performed with a Kratos Axis Ultra DLD instrument (Kratos Ltd.) using a monochromatic Al K α X-ray source (1486.6 eV, emission current: 10 mA, anode voltage: 15 kV). The instrument base pressure remained below 3.0×10^{-10} Torr. The work function was calibrated to a binding energy of 84.0 eV for metallic gold (Au 4f_{7/2}). The charge neutralizer system was used for all analyses. The charge neutralization was monitored with the help of the C 1s peak for adventitious carbon. Survey spectra and detail scans were recorded at a pass energy of 80 eV with 10 sweeps and an energy step of 1 eV. High-resolution spectra for the transitions C 1s, O 1s, Si 2p, and Si 2s were obtained at a pass energy of 20 eV and five sweeps each with an energy step of 0.1 eV. The analysis area was $\sim 300 \times 700 \mu\text{m}^2$. All spectra were recorded in the spectroscopy mode utilizing the hybrid lens mode. For each sample, at least three independent measurements were performed. The calculations of atomic percentage were performed from survey spectra corrected for transmission with the help of the commercial software CasaXPS (version 2.3.16, Casa Software Ltd.). The binding energies were calibrated using the C 1s peak for adventitious carbon at a binding energy of 284.8 eV, with an associated error of ~ 0.1 – 0.2 eV.³⁶

FTIR. Fourier-transform infrared spectroscopy (FTIR, Tensor II with Platinum ATR, Bruker) was applied to investigate chemical changes in PDMS, that is, hydrolysis and condensation reactions during the PDMS grafting process at room temperature. To maximize the silicon oxide surface area for the FTIR measurements, we took fumed silica (Aerosil 200, Evonik, surface area = 200 m² g⁻¹) and compressed it tightly on a glass slide. The compressed powder was oxygen-plasma cleaned at 300 W for 10 min. First, pure powder was investigated by FTIR. Thereafter, the powder was removed, and the attenuated total reflectance (ATR) crystal was cleaned. Second, a film of PDMS (MW 6000 g mol⁻¹) was spread on the crystal and investigated without the powder. Thereafter, the powder was applied on the PDMS and compressed tightly under a glass slide. The chemical changes were monitored by FTIR with time up to 24 h. The experiment was repeated twice to be sure that the results are repeatable. Each spectrum was recorded at a resolution of 1.4 cm⁻¹ by taking 200 scans. Recording each single spectrum thus took ~ 3 min. Penetration depth in the sample is ~ 1 – $2 \mu\text{m}$ at 1000 cm⁻¹. The penetration depth increases by an order of magnitude between 4000 and 400 cm⁻¹. The Bruker data acquisition software was used to correct the spectra for the absorption of ambient H₂O and CO₂ during the measurements.

UV–Vis. The light transmittance of the PDMS film for wavelengths ranging from 300 to 1500 nm was measured with an ultraviolet–visible light (UV–vis) spectrometer (Lambda 900, PerkinElmer).

UV Light Exposure. The UV stability of the PDMS film was investigated by illuminating the sample by UV-A light (intensity at the sample surface = 2.3 ± 0.3 mW cm⁻²) from a distance of 8 cm (light source: LQ-400, Dr. Gröbel UV-Elektronik GmbH). The illumination intensity was measured using a UV radiometer RM-12 with UV-A

sensor for a spectral range of 315–400 nm (Dr. Gröbel UV-Elektronik GmbH).

Stability against Acid/Base Solutions. The stability of the PDMS film in acid and base solutions was investigated by immersing the samples in 0.1 M aqueous solution of hydrochloric acid (HCl, pH = 1) or sodium chloride (NaOH, pH = 13), respectively, for 1 or 24 h.

Tape Adhesion. We performed the tape adhesion test following the ASTM D903 standard. As an adhesive tape we used a Tesa fabric tape (Gewebeband blue 2.75 m \times 19 mm). The tape was bonded to the substrate using a metallic roller with a diameter of 12.5 cm and a weight of 2.5 kg. After a settling time of 5 min, the tape was removed by pulling backward at a peel angle of 180° at a velocity of 15 cm min⁻¹. The mean adhesion force was recorded using a PCE-DFG N20 force gauge. The average adhesion force was determined from five independent measurements.

Ice Adhesion. Ice adhesion was measured using a home-built ice adhesion test apparatus. In brief, a force gauge (PCE-DFG N20, maximum measurable force of 20 N with an accuracy of $\pm 0.1\%$ of the measuring range) and a manual linear stage (XR50P/M 50 mm, Thorlabs) to move the sample were attached on an aluminum breadboard (Thorlabs). The whole setup was built in a freezing chamber (Mobicool FR40 compressor cooling system). First, the sample was attached to the linear stage and was let to cool for 5 min. Thereafter, we carefully deposited 50 μL water drops on the sample surface. After the drops were allowed to cool for 5 min, their freezing was initiated by touching them with a tiny ice crystal on the tip of tweezers. The drops were let to freeze in the chamber at -8 °C for different periods of time, from 10 min to 16 h. Thereafter, the chamber was opened from the top, and the sample with the ice drops was driven toward the force gauge tip at a velocity of $\sim 50 \mu\text{m s}^{-1}$. The temperature at the sample surface remained at -8 ± 1 °C during the measurements. The force F required to detach the ice drops from the sample surface was recorded. The contact point between the ice drop and the force gauge tip was set as close as possible to the substrate to be able to determine the shear forces reliably. Contact diameters of 50 μL water drops on different sample materials were determined with a contact angle goniometer. Thus, by knowing the contact area A of the drops on different samples, the lateral adhesion strength τ of ice was calculated according to $\tau = \frac{F}{A}$. The average adhesion strength of ice was determined from five individual measurements on each sample. When calculating the shear strength of ice, we assumed circular geometry for the contact line and that the contact area remained unchanged during freezing. We cannot exclude that the contact area expanded slightly during freezing; however, it is included in the given error margins.

RESULTS AND DISCUSSION

Effect of Rinsing Time on Contact Angle. The grafted PDMS film should only contain molecules tightly bound to the substrate. When investigating grafted PDMS films it is important to properly wash away the excess PDMS molecules that are not bound to the surface. Notably, careful rinsing with solvents, for example, with toluene, which is a good solvent for PDMS, does not remove all the excess, unbound PDMS molecules from the surface. After 10 s of rinsing the sample in a glass beaker filled with toluene, ethanol, and water, respectively, a film of PDMS, easily visible by the naked eye, remained on the glass surface (Figure S2). After 10–30 s of rinsing in the solvents, contact angle hysteresis and sliding angle both kept increasing with increasing rinsing time and were in the range of 1–6° (Table 1). After 20 s of rinsing, the PDMS layer thickness on silicon wafer measured by ellipsometry was 8 nm. For comparison, on the corresponding sample that was sonicated in the solvents and thus unbound PDMS was removed; the thickness of the PDMS coating was only ~ 3 nm. After 30 s of rinsing the contact angle hysteresis and sliding angle were $\sim 5^\circ$ lower as compared to the

Table 1. Water Repellency of PDMS Films Grafted to Glass after Washing off Excess PDMS by Rinsing in Solvents^a

rinsing time [s]	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
10	107 ± 1	107 ± 2	105 ± 2	2	<1
20	109 ± 1	108 ± 1	103 ± 2	5	5 ± 1
30	107 ± 1	109 ± 1	103 ± 4	6	6 ± 5
60	108 ± 1	110 ± 1	98 ± 2	12	10 ± 2
120	107 ± 1	111 ± 1	98 ± 2	13	11 ± 1

^aPDMS films were grafted at room temperature for 24 h, after which the excess PDMS was removed from the samples by rinsing in toluene, ethanol, and water, respectively, for 10–120 s in each solvent. PDMS molecular weight was 6000 g mol⁻¹.

corresponding samples sonicated in the solvents (Table 2a). The contact angle hysteresis and correspondingly the sliding

Table 2. Water Repellency of PDMS Films Grafted to Glass^a

(a) grafting time	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
0 min	0				
1 min	58 ± 5	60 ± 5	29 ± 6	31	
5 min	71 ± 3	73 ± 3	41 ± 1	32	
15 min	95 ± 1	97 ± 1	65 ± 1	32	
2 h	103 ± 1	106 ± 1	80 ± 1	26	
24 h	106 ± 1	109 ± 1	97 ± 1	12	12 ± 2
5 d	107 ± 1	109 ± 1	99 ± 1	10	7 ± 2
10 d	108 ± 1	109 ± 2	97 ± 2	12	11 ± 2
30 d	107 ± 1	110 ± 1	92 ± 2	18	18 ± 4
(b) temperature [°C]	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
-18	104 ± 1	108 ± 1	83 ± 4	25	
10	106 ± 1	109 ± 1	93 ± 1	16	22 ± 4
22–23 (RT)	106 ± 1	109 ± 1	97 ± 1	12	12 ± 2
100	105 ± 1	108 ± 1	95 ± 1	13	13 ± 2
(c) RH [%]	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
0.1	106 ± 1	109 ± 1	100 ± 1	9	11 ± 1
30–60	106 ± 1	109 ± 1	97 ± 1	12	12 ± 2
90	106 ± 1	108 ± 1	94 ± 1	14	11 ± 1
97–99	95 ± 3	98 ± 3	64 ± 4	34	

^a(a) PDMS films were grafted at room temperature for different periods of time. The excess PDMS was washed off by sonicating in toluene, ethanol, and water, respectively. The grafting time of 0 min represents wetting of a pristine glass surface after oxygen-plasma cleaning. (b) PDMS films were grafted at varying temperatures for 24 h. (c) PDMS films were grafted at room temperature for 24 h at varying RH. The advancing contact angles θ_a and receding contact angles θ_r were determined by the needle-in-sessile drop method. The sliding angle α is the angle at which 10 μ L drops started to move when the substrate was gradually inclined. PDMS molecular weight was 6000 g mol⁻¹.

angle started to saturate at $\sim 10^\circ$ after 1–2 min of rinsing in each of the solvents. This demonstrates that excess PDMS cannot be washed off easily by rinsing. Most likely some unbound PDMS remains on the surface after the rinse, and thus the coating remains in its lubricant-infused state.^{14,28–30}

The free molecules are held within the film by the grafted PDMS chains and act as a lubricant. Surface properties, therefore, depend on the amount of free PDMS within the film and vary as a function of the rinsing intensity and duration. To

remove all unbound PDMS as efficiently as possible, as a standard procedure through the work we first rinsed the samples in toluene and then sonicated them in toluene, ethanol, and water for 10 min in each solvent.

Reaction of PDMS with Oxide Surfaces. PDMS starts to bind to the glass surface immediately after it contacts the substrate at room temperature. Already after 1 min of contact time, the initially perfectly hydrophilic glass surface (contact angle $\theta \approx 0^\circ$ for water) becomes slightly water-repellent, displaying an advancing contact angle $\theta_a = 60 \pm 5^\circ$ and contact angle hysteresis of $31 \pm 2^\circ$. After 24 h of contact time, a hydrophobic PDMS film with $\theta_a = 109 \pm 1^\circ$ and contact angle hysteresis of $12 \pm 2^\circ$ was formed (Figure 1a–d, Table 2a). The film thickness was 2.8–3.1 nm; the thickness was measured by ellipsometry on silicon wafers (Table 3) and by AFM on glass from the elastic deformation of the film.

Prolonging the reaction time of PDMS on glass from 1 to 5 d and 10 d further increased the film thickness from 2.8 ± 1.1 nm to 4.3 ± 0.7 and 5.1 ± 0.7 nm, respectively, as measured by AFM. PDMS film thickness of ~ 4 nm (reaction time of 5 d) appears to yield the best water repellency with contact angle hysteresis of $10 \pm 1^\circ$ and sliding angle of $7 \pm 2^\circ$ for 10 μ L drops (Figure 1b,c, Table 2a). Higher film thickness yields increased pinning of water drops.

Molecular Weight of PDMS versus Film Thickness. In addition to the grafting of linear PDMS with molecular weight of 6000 g mol⁻¹, we grafted significantly lower and higher molecular weight linear PDMS varying from MW 770 to 117 000 g mol⁻¹. The optimum molecular weight for 24 h room temperature PDMS grafting is of the order of MW 10 000 g mol⁻¹ (Figure 1e). With lower or higher MW, the contact angle hysteresis of water starts to increase, Figure 1e and Table 3. In the case of low molecular weight, most likely, the attached PDMS chains are too short to be sufficiently flexible, and the influence of the underlying glass substrate is still noticeable; the contact angle hysteresis was 25–30° after letting the substrate react with a short-chain linear PDMS (MW = 770 g mol⁻¹). In the case of high MW, the chain length is above the threshold where molecule entanglement starts to occur, \sim MW 6000–7000 g mol⁻¹.³⁷ Entanglement reduces the mobility of the PDMS chains on the surface. Therefore, it increases the contact angle hysteresis and shifts wetting properties of the film toward those of cross-linked PDMS, where the chain mobility is restricted. Indeed, cross-linked silicone typically shows contact angle hysteresis as high as 35–50° for water (Figure 1d).^{38,39}

PDMS with a molecular weight of 6000 g mol⁻¹ contains ~ 80 Si–O units per one polymer chain (D number). Thus, the theoretical chain length for PDMS MW 6000 g mol⁻¹ is ~ 26 nm, when Si–O bond length = 0.163 nm, Si–O–Si bond angle = 150° , and dimethylsiloxane monomer weight ($(\text{CH}_3)_2\text{SiO}$) = 1.23×10^{-22} g. This simplified calculation is solely based on the geometry of the silicon–oxygen bonds⁶ in a theoretical case where the polymer chain is fully stretched. In reality, the chains are flexible and rather curly. Furthermore, they may orient parallel to the surface and not perpendicular. For PDMS MW 770 and 117 000 g mol⁻¹ the theoretical chain lengths are ~ 3 and 500 nm, respectively. Grafting of PDMS film includes scission of the polymer chains by attacking water molecules. Thus, the length of grafted PDMS chains is shorter than the original chain length of the PDMS fluid. In addition, because of the chain scission, the length distribution of individual chains grafted to the substrate is random. Grafted PDMS

Table 3. Water Repellency of PDMS Films Grafted to Glass at Room Temperature for 24 h using Different Molecular Weights for PDMS^a

grafting time [h]	MW[g mol ⁻¹]	ellipsometry thickness [nm]	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
24	770	1.1 ± 0.3	92 ± 1	95 ± 3	70 ± 2	25	
24	6000	3.1 ± 0.2	106 ± 1	109 ± 1	97 ± 1	12	12 ± 2
24	117 000	5.6 ± 0.2	113 ± 1	115 ± 1	75 ± 4	40	

^aFilm thicknesses were measured on silicon wafers by ellipsometry. Please note that the ellipsometry measurements do not contain the systematic error caused by the variations of the thickness of the native oxide layer.

chains are expected to lie on the surface and not to stand tall. Therefore, the thickness of the grafted PDMS films (Table 3) is much less than the theoretical chain length calculated based on the molecular weight of the used PDMS.

Sliding Angles of Different Liquids. The degree of pinning of a drop to the surface, that is, the lateral adhesion force F_{adh} , depends on the contact angle hysteresis, that is, the difference between the advancing θ_a and receding θ_r contact angles. For example, for 10 μ L water drops (comparable to a volume of a medium-sized raindrop⁴⁰) with a contact width $w = 3.2$ mm and a surface tension $\gamma = 0.073$ N m⁻¹, the contact angle hysteresis of 20° yields $F_{adh} \approx w\gamma(\cos \theta_r - \cos \theta_a) \approx 80$ μ N.^{38,41} Removing the drops from the surface by gravity, $F_G = mg \sin \alpha > F_{adh}$, where m is the mass of the drop, g is the gravitational acceleration, and α is the inclination angle of the substrate, would imply tilting of the substrate by more than 50°. Here, a 10 μ L water drop starts to move down the PDMS-coated glass surface as soon as the substrate is inclined by $\sim 10^\circ$ (Table 2a) indicating low $F_{adh} < 20$ μ N. The drops move slowly, ~ 10 μ m s⁻¹ when the inclination is below 15°. However, with higher inclinations, the drops reach a velocity on the order of a few millimeters per second (Supporting Information, Figure S3, Table S2). In addition to water, a variety of other liquids, including alkanes, oils, solvents, and fluorinated liquids, easily slide off from the PDMS-coated glass at inclinations below 10° (Figure 1f).

Stability and Applicability of the Coating. The PDMS films are stably bound. Water cannot replace the adsorbed PDMS, despite its high polarity and affinity to silicon oxide. Neither can the films be removed by sonication in organic solvents. This was tested by sonication of the samples for 10 min in water, ethanol, isopropyl alcohol, acetone, and toluene, after which contact angle hysteresis of water remained unchanged within the experimental accuracy of $\pm 2^\circ$. The films are 100% transparent, as verified by ultraviolet–visible light (UV–vis) spectroscopy (Supporting Information, Figure S4). The reason for the excellent transparency is the small refractive index mismatch of $\sim 3\%$ between PDMS and silicon oxide and the small film thickness. In contrast to porous water-repellent materials,²⁹ the PDMS films do not contain any light-reflecting structures. In addition, the films withstand UV illumination. After a 5 d exposure to UV-A light (intensity at the sample surface = 2.3 ± 0.3 mW cm⁻²), water repellency of PDMS-coated glass remained unchanged (Table 4).

The PDMS films are resistant to high temperatures due to the strong ionic character of the siloxane backbone. After being annealed in an oven at 100 °C for 5 h, any changes in the surface wettability could not be observed within the experimental accuracy. After being annealed at 400 °C for 5 h, the PDMS film still maintained its hydrophobic nature, and the contact angle hysteresis remained below 30° (Table 5). The increased hysteresis during the thermal treatment is associated with partial oxidation of the hydrophobic methyl

Table 4. Aging of Water-repellent PDMS Films Grafted to Glass at Room Temperature for 24 h^a

sample	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
pristine PDMS film	106 ± 1	109 ± 1	97 ± 1	12	12 ± 2
aged six months in the dark	105 ± 1	108 ± 1	98 ± 1	10	11 ± 1
aged 5 d under UV illumination	107 ± 1	109 ± 1	97 ± 1	12	12 ± 1

^aThe samples were aged in the dark at 22–23 °C and 30–60% relative humidity or illuminated with UV-A light (intensity = 2.3 ± 0.3 mW cm⁻²). PDMS molecular weight was 6000 g mol⁻¹.

Table 5. Temperature Stability of Water-repellent PDMS Films Grafted to Glass at Room Temperature for 24 h^a

sample	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
pristine PDMS film	106 ± 1	109 ± 1	97 ± 1	12	12 ± 2
annealed at 100 °C	106 ± 1	109 ± 1	98 ± 1	11	12 ± 1
annealed at 200 °C	105 ± 1	108 ± 1	88 ± 1	20	15 ± 2
annealed at 300 °C	104 ± 1	107 ± 1	81 ± 6	26	45 ± 15
annealed at 400 °C	99 ± 1	102 ± 1	74 ± 1	28	47 ± 4
annealed at 500 °C	0				

^aThe samples were annealed in air in an oven at varying temperatures for 5 h. PDMS molecular weight was 6000 g mol⁻¹.

side groups of PDMS.⁴² After being annealed at 500 °C, the glass surface became completely hydrophilic due to thermal degradation of the PDMS coating.

Immersion of the samples in acid or base solutions gradually degrades the PDMS coating (Table 6), which is expected considering the acid- and base-catalyzed chain opening and polymerization reactions used in industrial production of PDMS. After the PDMS-coated glass was stored for six months in the laboratory atmosphere, the wetting properties remained unchanged from those of the freshly prepared sample.

Furthermore, we tested the PDMS films without applying any solvents even in the washing step. Therefore, after applying PDMS on plasma cleaned glass for 24 h, we polished the sample surface with a paper tissue, so that all visible PDMS was removed (Video S4). The coating displayed even lower water contact angle hysteresis, $7 \pm 1^\circ$, than the sonicated samples. It is likely that a small amount of unbound PDMS remained on the sample surface after being polished, which is desirable in many applications, as the liquid repellency of the coating further improves.

Table 6. Stability of PDMS Films Against Acid/Base Solutions^a

immersion liquid/ immersion time	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
pristine PDMS film	106 ± 1	109 ± 1	97 ± 1	12	12 ± 2
H ₂ O/1 h	107 ± 1	109 ± 1	99 ± 2	10	11 ± 1
H ₂ O/24 h	105 ± 1	109 ± 1	97 ± 1	12	12 ± 1
HCl/1 h	101 ± 2	104 ± 1	88 ± 3	16	40 ± 2
HCl/24 h	51 ± 6	55 ± 7	26 ± 5	29	
NaOH/1 h	47 ± 9	54 ± 10	33 ± 5	21	
NaOH/24 h	40 ± 5	44 ± 2	0	44	

^aWater repellency of PDMS films after immersion in water (pH = 7) or in aqueous acid (0.1 M HCl in water, pH = 1) or base (0.1 M NaOH in water, pH = 13) solutions for 1 and 24 h. PDMS was grafted to glass at room temperature for 24 h. PDMS molecular weight was 6000 g mol⁻¹.

Because the 6000 g mol⁻¹ PDMS used here has a low viscosity (0.1 Pa s), thin PDMS films can be applied easily by a multitude of standard methods suitable for coating large surface areas, including painting, spraying, or roll-coating (Video S4). Complex objectives and heat-sensitive components can be coated, as the low surface tension $\gamma \approx 20$ mN m⁻¹ allows PDMS to easily wet almost all materials,¹ and thermal energy is not needed for the coating formation. Therefore, PDMS can react and bound to the substrate spontaneously even during storage or transport from production site to customer. To demonstrate the large-scale applicability of our

approach in potential applications, we coated different types of glass. In addition to the borosilicate glass used in the experiments, we coated soda-lime laboratory glass and glass vials with the PDMS films (Supporting Information, Video S5). In addition, other materials such as aluminum, stainless steel, polyester fabric, and paper can be coated after silica-modifying the substrates. To obtain the siloxane chemistry, we applied a nanometer-thin silica layer on the substrates by a gas-phase Stöber-like reaction³³ prior to applying the PDMS film (Supporting Information, Figure S5, Table S3, and Video S3).

The PDMS films on glass withstand cleaning with a cleaning tissue, abrasion with a rubber glove, scratching with a razor blade or a metal scouring sponge, and even repeated attachment and detachment of adhesive tape (Figure 2a, Video S6). Therefore, the PDMS films are mechanically stronger than most superhydrophobic or superoleophobic coatings (Supporting Information, Video S7).^{33,43} Lubricant-infused surfaces fail after the lubricant is depleted from the surface by, for example, continuous flow of water drops (Supporting Information, Video S1). The films show low adhesion to solids and liquids and can repel even super glue (Video S8), permanent markers (Figure 2b, Video S9), and spray paints (Figure 2c, Video S10). The excellent mechanical stability and the nonstick properties make grafted PDMS coatings a potential option to be used in antifouling and easy-to-clean applications.

The PDMS films can function as release layers for adhesive films and labels enabling their easy detachment and reattachment without losing adhesive properties of the glue. This was

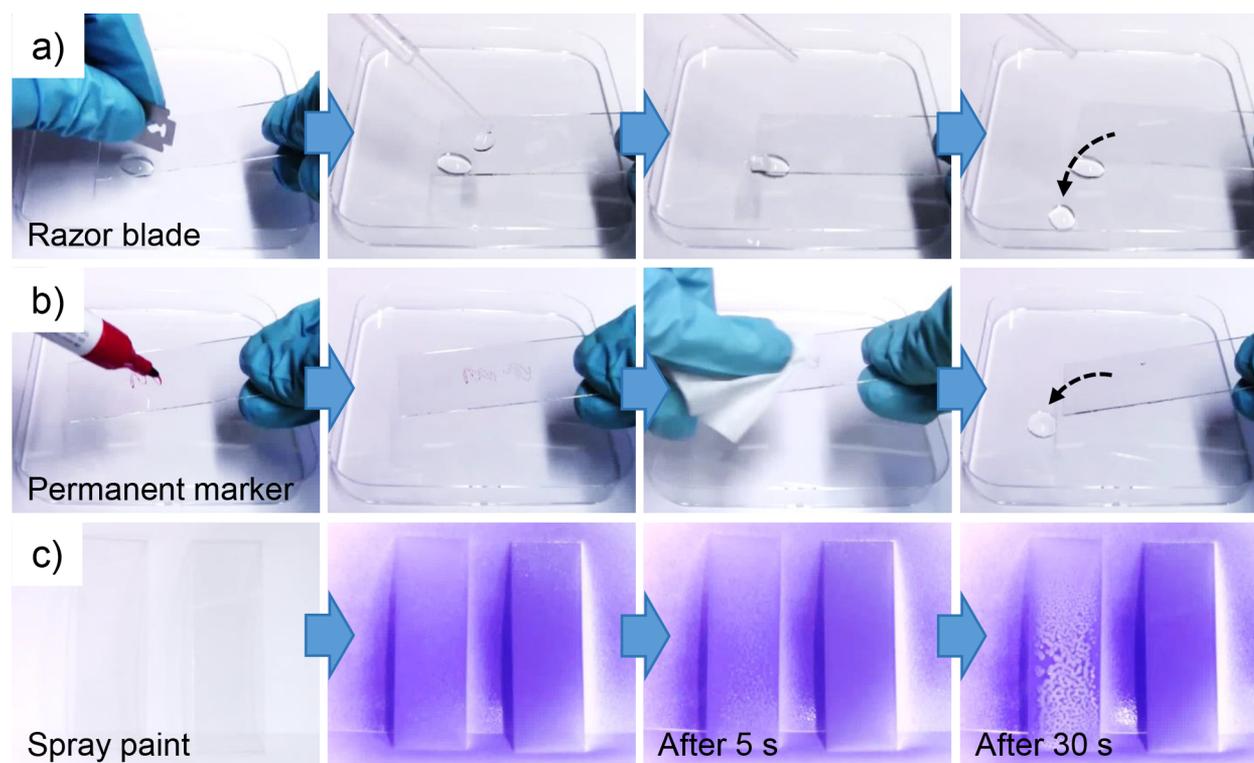


Figure 2. Photographs demonstrating stability and easy-to-clean properties of the PDMS films grafted to 1 mm thick soda-lime glass slides. (a) The films are tolerant against scratching with a razor blade (Supporting Information, Video S6) and (b) repel permanent markers allowing the surface to be cleaned with a paper tissue (Supporting Information, Video S9). The PDMS films allow easy sliding of water drops on their surface after the scratching or polishing with the tissue. (c) The PDMS films repel spray paint. Thirty seconds after spraying; the paint dewets the PDMS-coated glass (PDMS-coated glass on the left, uncoated glass on the right, Supporting Information, Video S10). The PDMS films were grafted at room temperature for 24 h. PDMS molecular weight was 6000 g mol⁻¹.

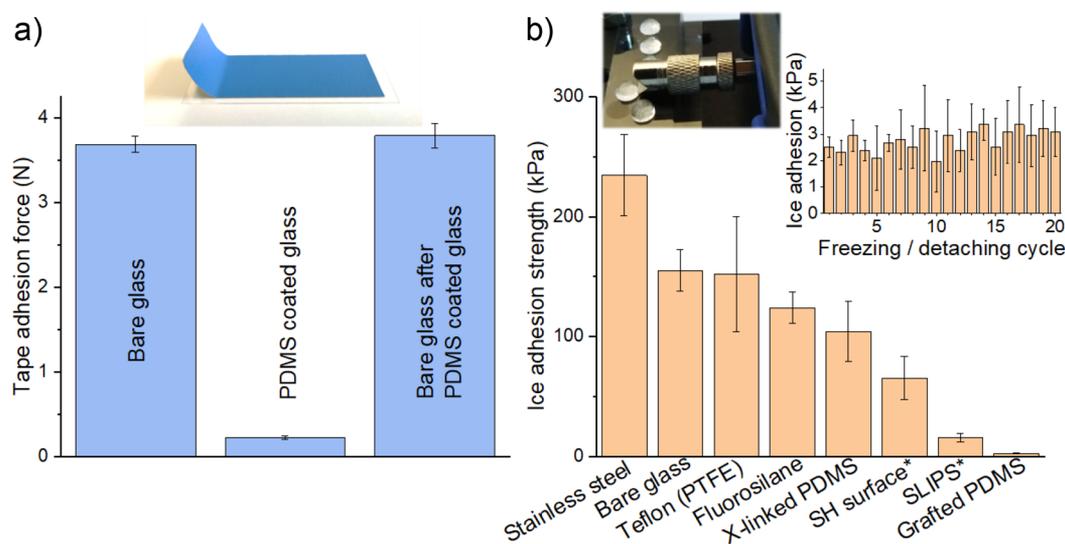


Figure 3. Tape and ice adhesion on grafted PDMS films on glass and on reference materials. (a) Mean adhesion force required to detach a 19 mm wide Tesa fabric tape (180° peel test) from uncoated glass, PDMS-coated glass, and from uncoated glass after the tape was first detached from the PDMS-coated glass and reattached to uncoated glass. (inset) Test tape attached to bare glass. The tape was bonded to the substrate using a metallic roller with diameter of 12.5 cm and weight of 2.5 kg. After a settling time of 5 min the tape was removed by being pulled backward at a peel angle of 180° at a velocity of 15 cm min^{-1} . (b) Ice adhesion strength measured on different materials at -8°C . Ice adhesion strength for superhydrophobic (SH) and slippery liquid-infused porous surface (SLIPS) were taken from refs 44 and 45 (*measured at -10°C). (insets) A photograph of the force gauge tip and ice drops on the PDMS-coated glass and ice adhesion strength results over 20 repeated freezing and detaching cycles of ice on the PDMS-coated glass. The PDMS films were grafted at room temperature for 24 h. PDMS molecular weight was 6000 g mol^{-1} .

demonstrated by attaching and measuring the force required to detach a Tesa fabric tape (180° peel angle) on a sample surface. The mean force required to move the tape from an uncoated glass was $3.7 \pm 0.1 \text{ N}$. On the PDMS-coated glass the mean adhesion force was significantly lower, only $0.22 \pm 0.02 \text{ N}$. That is, the PDMS coating lowered the adhesion force of the tape to glass by 94%. After the tape was removed from the PDMS-coated sample and reattached to the uncoated glass, the adhesion force was $3.8 \pm 0.1 \text{ N}$. This implies that the properties of the glue were not altered by the PDMS coating (Figure 3a).

The PDMS coatings significantly reduce ice adhesion on glass. The shear strength of ice drops on the PDMS-coated glass was as low as $2.7 \pm 0.6 \text{ kPa}$, that is, more than 98% less than ice adhesion on an uncoated glass, which was measured to be $155 \pm 17 \text{ kPa}$. Freezing of $50 \mu\text{L}$ drops that were used in the experiments takes only a few minutes. With our ice adhesion measurement setup full ice adhesion is reached already after freezing time of 10 min. We measured the ice adhesion strength on the PDMS-coated glass repeatedly 20 times on five individual spots. We marked target positions for the drops underneath the glass sample so that the drops could be placed at the same location each time. Within the 20 experiments, the ice adhesion strength remained unchanged within the experimental accuracy (Figure 3b, inset). Also, among other water-repellent test surfaces, including fluorinated materials and cross-linked PDMS, the grafted PDMS coatings showed remarkably low ice adhesion. For example, ice adhesion strength on cross-linked PDMS (Sylgard 184) was $104 \pm 25 \text{ kPa}$, that is, almost 40 times higher as compared to our grafted PDMS films (Figure 3b and Supporting Information, Figure S6 and Table S4).

PDMS Grafting Mechanism. The advantageous properties of the grafted PDMS films require that PDMS strongly binds to the substrate. PDMS itself does not contain reactive

groups. However, siloxane bonds (Si–O) can be hydrolyzed by water molecules to form reactive terminal hydroxyl groups. Therefore, for example, silicon dioxide is soluble in water.^{46–48} Dissolution of silicon dioxide in water is, however, relatively slow, on the order of 10 nm per year at room temperature.^{47,48} The good resistivity of silicon dioxide against an attack of water molecules arises from its structure, where Si^{4+} ions are in tetrahedral coordination with oxygen ions. Four water molecules are required to break the bonds to form fully hydrated silicic acid $\text{Si}(\text{OH})_4$.^{27,47,48} In addition, high connectivity of the glass network makes structural rearrangement difficult. With PDMS, the attack of a single water molecule is enough to break the Si–O bond to produce OH-terminated PDMS to initiate the grafting reaction via condensation with the surface OH groups. That is, hydrolyzing the siloxane backbone of PDMS to form hydroxyl-terminated PDMS chains enables the reaction with the surface silanols to form a stable, covalently bound PDMS film.

Considering the reactivity of PDMS with silicon oxide, one might question the ability of water to hydrolyze PDMS chains and claim that the surface reactions are due to the small amounts of residues that are left in PDMS from the manufacturing process. These residues may contain terminal OH groups that could theoretically cause the observed surface reactivity with silicon oxide. However, our results rule out that the PDMS surface reactions are due to the OH-terminated residues. Prolonged direct contact even with water slowly degrades the PDMS film (Table 7): nucleophilic attack of water molecules gradually breaks the siloxane bonds at the top of the film. The cleaved PDMS chains can restore the siloxane bonds via condensation, or the free ends of the cleaved chains can drift away from the surface. The degradation is extremely slow. Complete degradation of a few nanometer thick films takes several months. Thus, the degradation of grafted PDMS films in water is a strong indication that PDMS is hydrolyzed

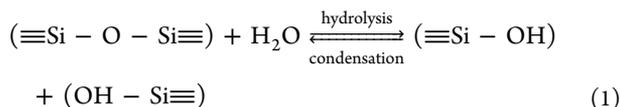
Table 7. Water Repellency of PDMS Films after Immersing in Water for 1–3 Months^a

immersion [months]	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
0	106 ± 1	109 ± 1	97 ± 1	12	12 ± 2
1	96 ± 2	98 ± 2	59 ± 2	39	19 ± 8
2	82 ± 6	86 ± 3	31 ± 3	55	
3	76 ± 1	79 ± 1	29 ± 4	50	

^aPDMS was grafted to glass at room temperature for 24 h. PDMS molecular weight was 6000 g mol⁻¹.

by the attack of water molecules. Eventually, prolonged direct contact with water will completely degrade the PDMS coatings.

We propose a reaction that takes place at room temperature and does not require an acid catalyst. Our results hint that the reaction between PDMS and silicon oxide is initiated by hydrolysis of the siloxane bonds of PDMS via a nucleophilic attack of the oxygen contained in water according to eq 1. The two Si–OH-terminated chain ends can then link to surface silanol groups or to another cleaved PDMS chain (Figure 4). An example of such a hydrolysis reaction is the dissolution of silicon dioxide in water at room temperature.^{46–48}



Notably, the reaction is reversible; that is, the silanol groups formed by hydrolysis can condense to restore the siloxane bond and release a water molecule. Indeed, the condensation reaction is known in the context of silicon wafer bonding.^{47,49–51} Thus, it can be expected that surface-exposed siloxane bonds of PDMS hydrolyze by the surface-bound water to form two reactive silanol groups. These silanol groups then readily condense with the surface silanols to covalently bond PDMS to the substrate. Our data consistently support that this happens at room temperature and below (Table 2b).

The Effect of Grafting Temperature on the Coating Quality. We also tested how ambient temperature affects the coating properties. Therefore, we fabricated control PDMS films at varying temperatures between –18 and +100 °C (Table 2b).^{7,8,24} PDMS binding to the glass substrate is pronounced even at temperatures significantly below the room temperature. The adsorption is, however, faster at higher temperatures.^{8,14} For example, contacting glass with PDMS at 10 °C for 24 h yields a 4° higher contact angle hysteresis as compared to the corresponding sample prepared at room

temperature. One reason for the faster reaction at high temperatures is likely removal of excess molecular water from the surface. A too-high amount of surface-bound water blocks the surface silanols and thus prevents hydrolyzed PDMS from establishing chemical bonds at the surface. However, after 24 h of grafting time, contact angle hysteresis on the films prepared at 100 °C^{7,8} did not deviate from the samples prepared at room temperature (Table 2b and Table 8). It is worth pointing out that, at higher temperatures above 200 °C used by other groups,¹⁴ the grafting reaction may be different from the room temperature grafting and may include thermal degradation of the methyl side groups of PDMS.

Grafting with Cyclic PDMS. If our explanation is correct, cyclic PDMS should also bind to glass. Therefore, we used low molecular weight cyclic PDMS (decamethylcyclopentasiloxane, D5, molecular weight = 371 g mol⁻¹, Supporting Information, Figure S7) to investigate whether the terminal methyl groups of PDMS play a role in the reaction with silicon oxide. A few drops of the cyclic PDMS were deposited on the sample surface and were let to spread spontaneously. The sample was stored in a plastic container in a similar way to the samples with linear PDMS. Despite the fact that the cyclic PDMS was volatile, even after 24 h, some PDMS remained at the sample surface, as the container slowed down the evaporation. The surface reaction appears to be analogous to the linear PDMS; that is, water repellency of the glass surface starts to increase immediately after contact with the PDMS (Table 9). After 24 h of grafting time, the contact angle hysteresis with low MW linear PDMS (770 g mol⁻¹) was ~25°, and with the cyclic PDMS it was ~30°. Likely, in both cases, the grafted PDMS molecules are too short to fully cover the surface or to be sufficiently flexible. Indeed, the analogy of the surface reaction between the linear and cyclic PDMS indicates that the reaction occurs via hydrolysis of the siloxane backbone of PDMS, followed by condensation with the surface silanols. Possible hydrolysis of the methyl side groups can be excluded, as such a reaction would rapidly turn the PDMS film completely hydrophilic when contacting with water.

Grafting PDMS to Dehydroxylated Silicon Oxide. To get more information on the relevance of the surface silanols in the grafting of PDMS, we investigated the formation of coatings on partially dehydroxylated silicon oxide surfaces. Fully hydroxylated silicon dioxide surfaces have a hydroxyl group density of ~5 OH nm⁻².²⁵ Dehydroxylation of silicon dioxide surfaces, that is, removal of surface OH groups, starts at ~200 °C via associative desorption of the OH groups (Figure 5) leading to the formation of siloxane bridges (≡Si–O–Si≡) and water condensation at the surface.²⁵ We

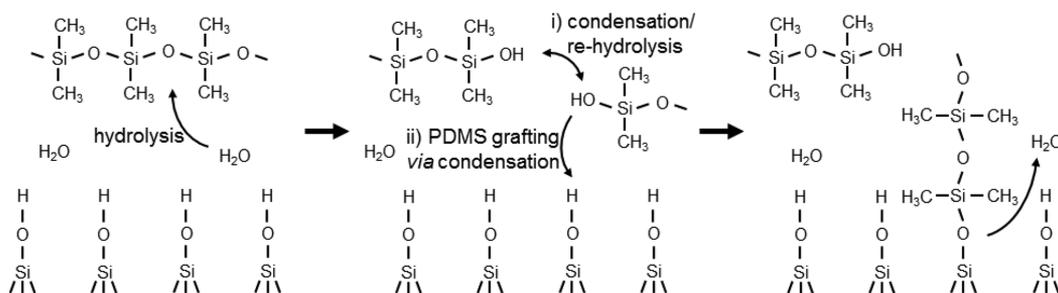


Figure 4. Proposed grafting reaction of PDMS to silicon oxide at room temperature. Covalent attachment of linear PDMS chains to the surface occurs via hydrolysis and condensation reactions. The scission of a single PDMS chain by hydrolysis consumes a single water molecule. Ideally, if both of the hydrolyzed chain ends react with the oxide surface, two water molecules are released.

Table 8. Water Repellency of PDMS Films Grafted at Room Temperature and 100 °C^a

substrate	grafting <i>T</i> [°C]	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
glass	22–23	106 ± 1	109 ± 1	97 ± 1	12	12 ± 2
glass	100	105 ± 1	108 ± 1	95 ± 1	13	13 ± 2
Si wafer	22–23	106 ± 1	109 ± 1	99 ± 1	10	17 ± 2
Si wafer	100	106 ± 1	108 ± 1	101 ± 1	7	10 ± 1

^aWater repellency of PDMS films grafted to glass and silicon wafer at room temperature and 100 °C for 24 h. PDMS molecular weight was 6000 g mol⁻¹.

Table 9. Water Repellency After Grafting of Cyclic Silicone^a

grafting time	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
15 min	65 ± 2	71 ± 1	41 ± 3	30	
24 h	79 ± 2	82 ± 6	52 ± 4	30	
* ^b	~0				
** ^c	8 ± 1				

^aWater repellency of glass surface after grafting of cyclic silicone decamethylcyclopentasiloxane (DS) at room temperature. ^b*Glass surface after oxygen-plasma cleaning and without any DS grafting. Water perfectly spreads on the surface. ^c**Glass surface after oxygen-plasma cleaning and sonicating in toluene, ethanol, and water, 10 min in each solvent, respectively, without any DS grafting. θ_a and θ_r cannot be determined on bare glass surfaces due to the spontaneous spreading of water drops.

annealed silicon wafers in air at 500 and at 900 °C for 5 h to reduce the number of surface silanols. At first, physically adsorbed water is removed. This is followed by condensation of surface silanols to siloxane bridges. According to Agzamkhodzhaev et al.,⁵² the surface OH-group density is only 0.66 OH nm⁻² after being annealed in air at 900 °C. Recovery of the surface OH groups occurs via dissociative adsorption of water (Figure 6). The process involves the breaking of the siloxane bridges and is typically extremely slow at room temperature.

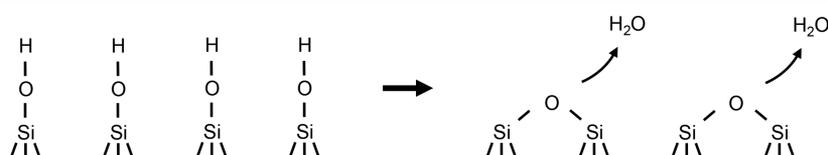
Recovery of the surface OH groups can take even five years.²⁵ Even so, room-temperature grafting of PDMS on dehydroxylated surfaces is pronounced: after 24 h of grafting the sample that was annealed at 500 °C exhibited similar or even better water repellency as compared to the corresponding oxygen-plasma cleaned sample; that is, the contact angle hysteresis was less than 10° (Table 10). The sample annealed at 900 °C displayed reduced, but still good, water repellency with $\theta = 103 \pm 1^\circ$ and contact angle hysteresis of $26 \pm 1^\circ$ (Table 11a) after PDMS grafting. The reason for the lower water repellency of the sample annealed at 900 °C is the reduced density of grafted PDMS chains at the surface, which was verified by XPS from the amount of elemental carbon, which originates from the methyl side groups of grafted PDMS (Table 11b and Table 12), on the samples. Furthermore, XPS analysis on partially dehydroxylated (annealed in air at 900 °C for 5 h) and hydroxylated (oxygen-plasma cleaned) silicon oxide surfaces shows that increasing the grafting time from 1 to 5 d increased the amount of bound PDMS by ~10% on both

samples (Table 11). This is a clear indication that the grafting density on one surface compared to the other remained unchanged, and thus the already attached PDMS chains appear to grow linearly.

Growth of the Coating. To determine the PDMS film thickness, we used AFM force spectroscopy. On the pure glass reference surface, the tip directly jumped into the solid surface (red line in Figure 7a). On the PDMS-coated surfaces, however, the tip could still move at a negative force over a couple of nanometers before the force turned repulsive again. The shape of the force curves is typical for liquid polymer films.^{53–55} The PDMS film thickness was estimated from the distance between the first snap-in position during the approach and the next crossing of the *x*-axis (dashed vertical lines in Figure 7b–d). The elastic deformation of the remaining PDMS under the tip and the exact shape of the meniscus after the snap-in adds a systematic error of ±1 nm to the measured distances. The AFM experiments show that the PDMS film thickness grows from 2.8 ± 1.1 nm after 1 d of grafting to 5.1 ± 0.7 nm after 10 d of grafting, and the adhesion force between the sample surface and the silicon tip of the AFM cantilever is suppressed from 7.1 ± 0.7 to 2.6 ± 0.4 nN, respectively (Figure 7a–d). To analyze the chemical nature of the bond we performed FTIR measurements on densely packed silicon oxide particles (surface area = 200 m² g⁻¹) immersed in PDMS (Figure 8 and Supporting Information, Figure S8). The absorption band from the siloxane bonds of PDMS at 1000–1130 cm⁻¹ first reduce and then increase in line with the proposed hydrolysis and condensation reactions of PDMS at the oxide surface.

Surface-bound water plays an important role in the beginning of the reaction by hydrolyzing PDMS in the vicinity of the oxide surface. Since PDMS contains ~100 ppm molecular water²⁴ capable of diffusing through the film,¹ indeed, the grafting reaction should not be limited to the vicinity of the oxide surface. Instead, as indicated by our results, the growth of the bound PDMS chains should continue at the distance of several nanometers above the surface via random hydrolysis and condensation reactions (Figures 4 and 7e, Table 11).

Another hint of the reactions between PDMS and silicon oxide was given by Sun et al.,¹⁷ who investigated the interaction of an AFM tip and a silicon oxide surface immersed in a PDMS fluid. They observed that, initially, an oscillatory interaction became monotonically repulsive after 10 h. Such a

**Figure 5.** Dehydroxylation of silicon oxide surface via associative desorption of surface silanols at temperatures above 200 °C.

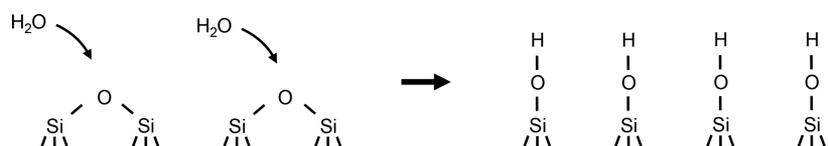


Figure 6. Recovery of surface silanols on silicon oxide via dissociative adsorption of water.

Table 10. Water Repellency – Grafting After Different Pre-Treatments^a

substrate	treatment	grafting time [d]	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
glass	O ₂ plasma	1	106 ± 1	109 ± 1	97 ± 1	12	12 ± 2
glass	annealed at 500 °C	1	106 ± 1	108 ± 1	101 ± 1	7	12 ± 2
Si wafer	O ₂ plasma	1	106 ± 1	109 ± 1	99 ± 1	10	17 ± 2
Si wafer	annealed at 500 °C	1	107 ± 1	108 ± 1	100 ± 1	8	14 ± 2

^aWater repellency of PDMS films grafted to glass and silicon wafers at room temperature. Different pre-treatments were applied to the substrates prior to PDMS grafting: the substrates were either hydroxylated by oxygen-plasma cleaning or partially dehydroxylated by being annealed in air in an oven at 500 °C for 5 h. PDMS molecular weight was 6000 g mol⁻¹.

Table 11. PDMS Films Grafted to Hydroxylated and Dehydroxylated Silicon Oxide^a

(a)	substrate	treatment	grafting time	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
	Si wafer	O ₂ plasma	no	0				
	Si wafer	O ₂ plasma	1 d	106 ± 1	109 ± 1	99 ± 1	10	17 ± 2
	Si wafer	O ₂ plasma	5 d	106 ± 1	108 ± 1	100 ± 1	8	8 ± 1
	Si wafer	annealed at 900 °C	1 d	103 ± 1	106 ± 1	80 ± 1	26	
	Si wafer	annealed at 900 °C	5 d	107 ± 1	109 ± 2	96 ± 2	13	27 ± 3
(b)	substrate	treatment	grafting time [d]	C [%]	O [%]	Si [%]	C/(O+Si)	
	Si wafer	O ₂ plasma	no grafting	5.6 ± 0.4	44.3 ± 0.7	50.1 ± 0.8	0.06	
	Si wafer	O ₂ plasma	1	19.9 ± 0.4	31.4 ± 0.6	48.7 ± 0.2	0.25	
	Si wafer	O ₂ plasma	5	21.6 ± 0.1	28.8 ± 0.4	49.7 ± 0.3	0.28	
	Si wafer	annealed at 900 °C	1	14.5 ± 0.2	43.4 ± 0.2	42.1 ± 0.3	0.17	
	Si wafer	annealed at 900 °C	5	16.1 ± 0.4	41.1 ± 0.2	42.8 ± 0.3	0.19	

^aPDMS films grafted to hydroxylated and dehydroxylated silicon oxide at room temperature. (a) Water repellency of PDMS films grafted to silicon wafers for 1 and 5 d. Different pre-treatments were applied to the substrates prior to the PDMS grafting: the substrates were either hydroxylated by oxygen-plasma cleaning or partially dehydroxylated by being annealed in air in an oven at 900 °C for 5 h. (b) Elemental composition of silicon wafer surfaces before and after the PDMS grafting. The relative percentages of elemental carbon (C), oxygen (O), and silicon (Si) were determined by XPS from the C 1s, O 1s, and Si 2p_{3/2} high-resolution peaks, respectively. PDMS molecular weight was 6000 g mol⁻¹.

Table 12. Elemental Composition of Silicon Oxide Surfaces Before and After PDMS Grafting^a

substrate	treatment	grafting time [d]	C [%]	O [%]	Si [%]
Si wafer		no grafting	9.7 ± 0.3	26.6 ± 0.1	63.6 ± 0.3
Si wafer	O ₂ plasma	no grafting	5.6 ± 0.4	44.3 ± 0.7	50.1 ± 0.8
Si wafer	O ₂ plasma	1	19.9 ± 0.4	31.4 ± 0.6	48.7 ± 0.2
Si wafer	annealed at 500 °C	1	21.2 ± 0.3	36.4 ± 1.0	42.4 ± 0.9
Si wafer	annealed at 900 °C	1	14.5 ± 0.2	43.4 ± 0.2	42.1 ± 0.3

^aElemental composition of silicon wafer surfaces before and after PDMS grafting at room temperature for 24 h. Different pre-treatments were applied to the substrates prior to PDMS grafting: the silicon wafer surfaces were either oxygen-plasma cleaned or annealed in air in an oven at 500 or 900 °C for 5 h. The relative percentages for elemental carbon (C), oxygen (O), and silicon (Si) were determined by XPS from the C 1s, O 1s, and Si 2p_{3/2} high-resolution peaks, respectively. PDMS molecular weight was 6000 g mol⁻¹.

repulsive force is an indication for the bound PDMS chains. Indeed, the reaction of PDMS and silicon oxide is generic. Breaking a single PDMS chain via hydrolysis—to create two hydroxyl-terminated PDMS chains readily reactive with the surface silanols—only requires a single water molecule. A sufficient amount of molecular water to initiate the grafting reaction at room temperature is always available at the silicon oxide surface as a layer of physisorbed water.^{24,25} In addition, when a hydrolyzed PDMS chain binds to the oxide surface via condensation, water is released (Figure 4). Thus, the availability of molecular water does not limit the grafting reaction even at a very low relative humidity (Table 2c).

Furthermore, our strategy does not require a fully hydroxylated or clean silicon oxide surface. The grafting reaction yields a drastic decrease in contact angle hysteresis down to ~10° also on partially dehydroxylated surfaces (Tables 10–12) and even on surfaces on which the silanol groups are covered by a contaminant layer, for example, hydrocarbons adsorbed from air (Table 13 and Supporting Information, Table S5).

The amount of grafted PDMS on the dehydroxylated surfaces does not correlate with the number of surface hydroxyl groups. The data reveal that the difference in the amount of elemental carbon detected on the surfaces, which

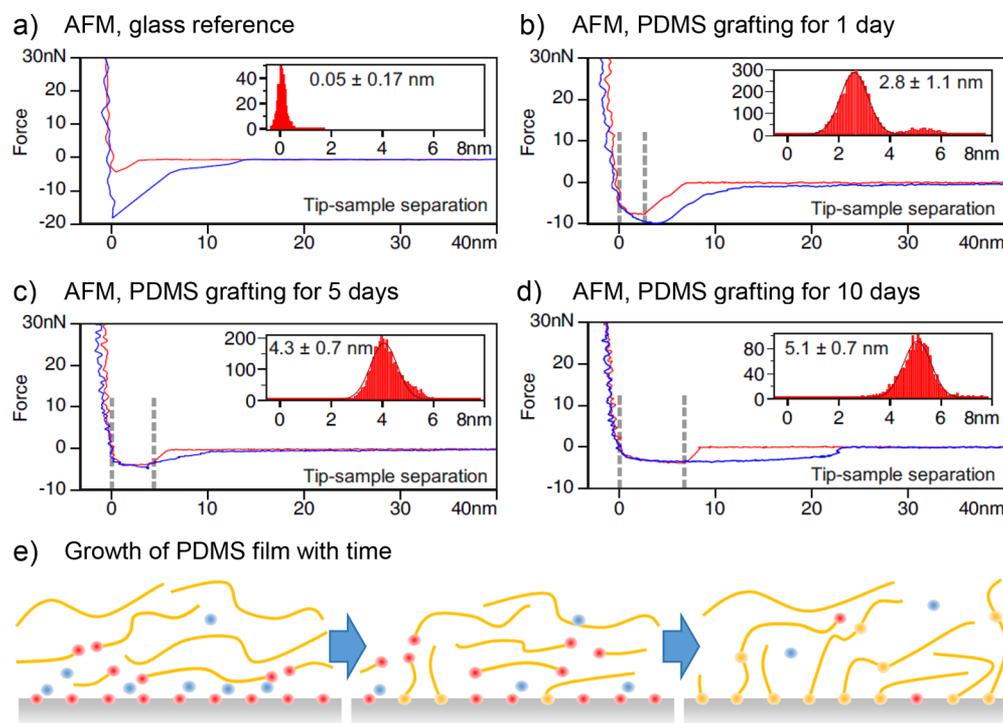


Figure 7. Grafting PDMS to silicon oxide. (a) Representative AFM force curves recorded while approaching to (red color) and retracting from (blue color) pristine oxygen-plasma cleaned glass, adhesion force = 17 ± 3 nN, and room-temperature grafted PDMS films on glass for (b) 1 d, film thickness = 2.8 ± 1.1 nm, adhesion force = 7.1 ± 0.7 nN; (c) 5 d, film thickness = 4.3 ± 0.7 nm, adhesion force = 3.3 ± 0.3 nN; and (d) 10 d, film thickness = 5.1 ± 0.7 nm, adhesion force = 2.6 ± 0.4 nN. (insets) Histogram and average of PDMS film thickness after the different grafting periods. In total 4096 force curves were recorded on each PDMS-coated sample. (e) Schematic of the PDMS film growth mechanism. Yellow strings indicate PDMS molecules. Blue dots indicate molecular water, and red dots indicate hydroxyl groups at the substrate or the chain ends of hydrolyzed PDMS. Yellow dots indicate established chemical bonds via condensation of hydroxyl groups. In (a–d) PDMS molecular weight was 6000 g mol^{-1} .

originates from the methyl side groups of PDMS, is much less than the difference in the OH-group density at the fully hydroxylated and annealed surfaces. On the sample annealed at $500 \text{ }^\circ\text{C}$ the amount of elemental carbon was even higher, $21.2 \pm 0.3\%$, than on the corresponding oxygen-plasma cleaned sample on which the amount of carbon was $19.9 \pm 0.4\%$ (Table 12). Likely, in this case, the removal of excess physisorbed water by annealing facilitated the PDMS grafting. In line with this result, both on glass and silicon wafer substrates, the contact angle hysteresis of water was $2\text{--}5^\circ$ lower on the annealed samples at $500 \text{ }^\circ\text{C}$ as compared to the oxygen-plasma cleaned samples (Table 10). This indicates that the room-temperature grafting reaction of PDMS on dehydroxylated silicon oxide surfaces involves siloxane bridge opening followed by covalent bonding of hydrolyzed PDMS to the surface (Figure 9). That is, surface hydroxyl groups are not necessarily needed for the grafting reaction on silicon oxide. Thus, the results indicate that hydrolyzed PDMS can open siloxane bonds at silicon oxide surfaces (Figure 9) and even replace chemisorbed contaminants (Figure 10) due to the far stronger ionic character of the Si–O bonds (50%) as compared to the C–O bonds (22%, Supporting Information, Table S1).

On both the plasma-cleaned and the annealed samples extended grafting time from 1 d to 5 d further increases the amount of grafted PDMS. In both cases, the amount of carbon increased by $\sim 10\%$. This indicates that the grafting density ratio between the samples remains unchanged, and the increase in the amount of carbon is primarily due to the

linear growth of the already attached PDMS chains (Table 11). A likely reason is that, on a dehydroxylated surface, the opening of a siloxane bridge and bonding of a hydrolyzed PDMS does not release any water (Figure 9), and, therefore, PDMS hydrolysis in the vicinity of the surface—and thus establishing new grafting sites—is limited by the availability of molecular water.

Grafting PDMS to Contaminated Glass Surface. To investigate whether PDMS can also be grafted to surfaces where silanols are covered by organic impurities, we applied PDMS to glass that was not exposed to oxygen-plasma cleaning. The glass surface thus contained a native contamination layer of low-surface-energy species, such as hydrocarbons. Such contaminations adsorb to the surface from the atmosphere,²⁶ cover the surface silanols, and thus lower the surface energy. Therefore, prior to grafting, water drops on the glass displayed a finite static contact angle $\theta = 43 \pm 3^\circ$. After 24 h of PDMS grafting at room temperature, the surface became water-repellent with $\theta = 103 \pm 1^\circ$ and a contact angle hysteresis of $26 \pm 1^\circ$ (Table S5). After prolonged grafting time of 5 and 10 d, the contact angle hysteresis decreased to $14 \pm 2^\circ$ and $10 \pm 2^\circ$, respectively (Table 13). That is, the hysteresis became as low as on plasma-cleaned glass after PDMS grafting.

PDMS can also be grafted to a glass surface pretreated with chemical vapor deposition of trimethylchlorosilane. Prior to PDMS grafting, the surface silanols on the CVD-coated sample were occupied by methyl groups. Therefore, the surface was repellent to water with $\theta = 84 \pm 1^\circ$. After 5 d of PDMS grafting at room temperature, the contact angle increased to θ

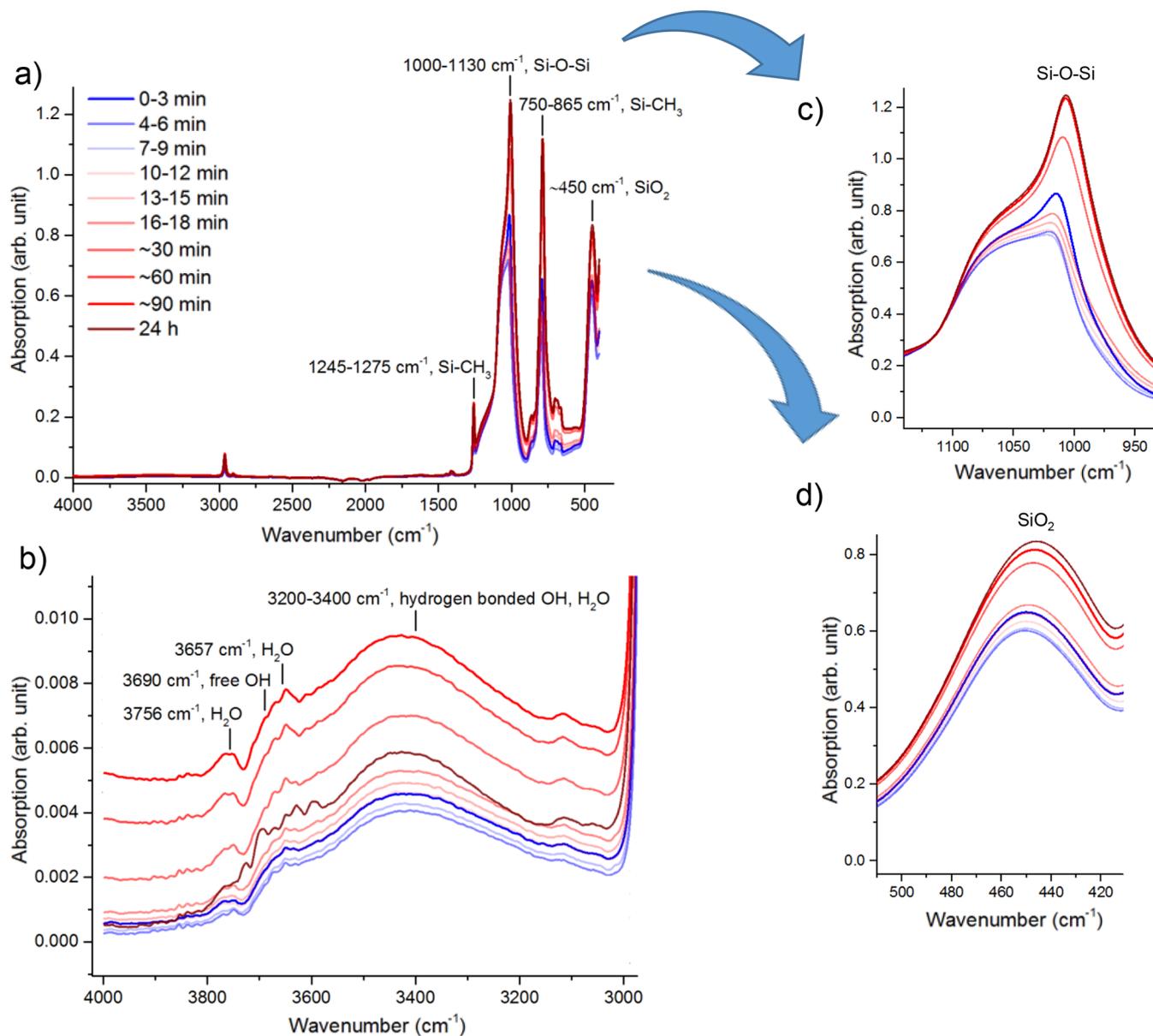


Figure 8. Monitoring chemical changes by FTIR during PDMS grafting to silicon oxide particles at room temperature. (a) Evolution of the FTIR absorption spectrum after contacting PDMS with silicon oxide particles. (b) Evolution of the absorption bands of hydroxyl groups and water during the grafting reaction. (c, d) Magnifications of the characteristic bands of Si–O–Si and SiO₂ shown in (a). Prior to the experiments the particles were densely packed and oxygen-plasma cleaned to provide a sufficiently large surface area for the grafting reaction to enable detection of the chemical changes in PDMS during the reaction. PDMS molecular weight was 6000 g mol⁻¹.

Table 13. Water Repellency of PDMS Films Grafted to Contaminated Glass^a

grafting time [d]	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
1	103 ± 1	107 ± 1	81 ± 1	26	
5	106 ± 1	108 ± 1	94 ± 2	14	17 ± 10
10	106 ± 1	109 ± 1	99 ± 1	10	16 ± 6

^aWater repellency of PDMS films grafted to contaminated glass at room temperature for 1–10 d. The glass surface was not cleaned by oxygen-plasma prior to the grafting; that is, most of the surface silanols were occupied by atmospheric contaminants such as hydrocarbons. PDMS molecular weight was 6000 g mol⁻¹.

= 100 ± 1° (Table 14). These data indicate that PDMS can even substitute part of the methyl groups on the oxide surface.

That is likely caused by the lower electronegativity of silicon as compared to carbon, that is, oxygen–carbon bonds are replaced by more ionic oxygen–silicon bonds (Figure 10 and Supporting Information, Table S1).

SUMMARY

In summary, our environmentally friendly method to fabricate transparent liquid-, adhesive-, and ice-repellent coatings that are mechanically stable and can be easily applied on a large scale does not require the use of any solvents, nor does it release any chemicals or hazardous byproducts to the environment. The coating shows advantageous properties including low sliding angles below 10° for various liquids, extremely low ice adhesion strength of 2.7 ± 0.6 kPa, and easy cleanability. Therefore, we anticipate our work to open new

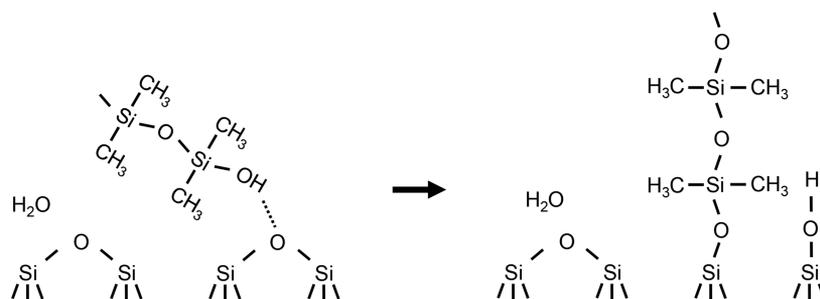


Figure 9. Proposed mechanism of PDMS grafting to dehydroxylated silicon oxide surface at room temperature. The opening of the siloxane bridges at the surface is initiated by hydroxylated PDMS. The bonding reaction on the dehydroxylated surface does not release molecular water. Thus, lack of molecular water at the surface slows the grafting reaction as compared to the hydroxylated surface presented in Figure 4. Graffius et al.²⁴ explained bonding of PDMS on dehydroxylated silicon oxide at an elevated temperature of 100 °C by a direct reaction between the PDMS backbone and siloxane bridges at the surface. Because of the extremely slow recovery of surface silanols at room temperature,²⁵ we propose an alternative mechanism to explain the PDMS grafting to dehydroxylated silicon oxide surfaces.

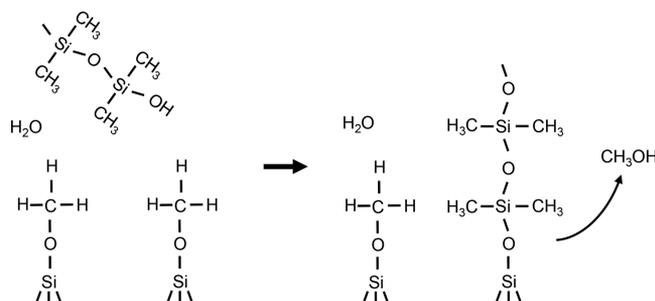


Figure 10. Proposed mechanism of PDMS grafting to a contaminated silicon oxide surface at room temperature.

Table 14. Water Repellency of PDMS Films Grafted to Methylated Glass^a

grafting time [d]	θ [deg]	θ_a [deg]	θ_r [deg]	$\theta_a - \theta_r$ [deg]	α [deg]
0	84 ± 1	86 ± 1	67 ± 1	19	
1	88 ± 1	92 ± 1	66 ± 1	26	
5	100 ± 1	103 ± 1	75 ± 2	28	

^aWater repellency of PDMS films grafted to methylated glass surface at room temperature. The grafting time = 0 d presents wetting of a glass surface after CVD of trimethylchlorosilane. PDMS grafting was applied on the pristine methylated surface, where surface silanols are occupied by the methyl groups. PDMS molecular weight was 6000 g mol⁻¹.

avenues in tailoring surfaces with silicones. Indeed, knowledge on the reactivity of PDMS is crucial in understanding the formation of PDMS coatings and their properties, polymer filler interactions, degradation of silicone rubber in humid environments,¹⁸ or degradation of PDMS in nature.⁵⁶

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.9b03223>.

Video S1 – Description in Supporting Information PDF (MP4)

Video S2 – Description in Supporting Information PDF (MP4)

Video S3 – Description in Supporting Information PDF (MP4)

Video S4 – Description in Supporting Information PDF (MP4)

Video S5 – Description in Supporting Information PDF (MP4)

Video S6 – Description in Supporting Information PDF (MP4)

Video S7 – Description in Supporting Information PDF (MP4)

Video S8 – Description in Supporting Information PDF (MP4)

Video S9 – Description in Supporting Information PDF (MP4)

Video S10 – Description in Supporting Information PDF (MP4)

Discussion of surface water repellency, illustrated structure of PDMS, photos of surfaces coated with PDMS, plot of transmittance versus wavelength, absorption spectra, selected bond lengths, contact angle hysteresis, wettability and ice adhesion strength, descriptions of MP4 Videos (PDF)

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Notes

The authors declare no competing financial interest.

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