

Simple and Improved Approaches to Long-Lasting, Hydrophilic Silicones Derived from Commercially Available Precursors

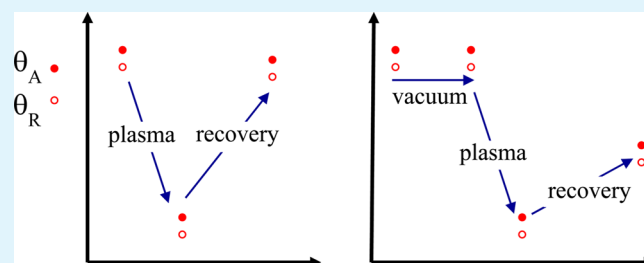
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ABSTRACT: Three types of commercially derived methylsilicone materials, Sylgard-184, Q^VQ^H (an MQ-based silicone containing no dimethylsiloxane, D units), and D^VD^H (a D-based silicone with no additives), were judiciously chosen to study the conditions under which long-lasting hydrophilicity after oxygen plasma treatment can be obtained. A 30 s plasma treatment time under controlled conditions was found to be optimal in terms of achieving the lowest initial advancing and receding contact angles of $\theta_A/\theta_R = 10^\circ/5^\circ$ with undetectable surface damage. Vacuum treatment, a necessary step prior to plasma ignition that has been overlooked in previous studies, as well as room temperature curing were explored as means to remove low molecular weight species. For thin films (a few micrometers), 40 min vacuum treatment was sufficient to achieve low dynamic contact angles of $\theta_A/\theta_R = 51\text{--}56^\circ/38\text{--}43^\circ$ on all three types of silicones measured more than 30 days after the plasma treatments. These values indicate superior hydrophilicity relative to what has been reported. The small and slow rise in contact angle over time is likely caused by the intrinsic nature of the silicone materials, i.e., surface reorientation of hydrophilic functional groups to the bulk and condensation of surface silanol groups, and is thus unavoidable. For thick films (~ 1 mm), room temperature curing in addition to vacuum treatment was required to reduce hydrophobic recovery and to achieve long-lasting hydrophilicity. The final contact angles for thick samples were slightly higher than the corresponding thin film samples due to the greater “reservoir” depth and migration length for mobile species. In particular, Sylgard exhibited inferior performance among the thick samples, and we attribute this to the additives in its commercial formulation. Furthermore, unlike polydimethylsiloxane-based silicones, Q^VQ^H does not contain equilibration products of the D_n-type; its thin films perform as well as those of Sylgard and D^VD^H. Silicones without D units are promising materials with intrinsically low hydrophobic recovery characteristics and long-lasting hydrophilicity after oxygen plasma treatment.

KEYWORDS: silicone, PDMS, Sylgard, contact angle, hydrophilization, hydrophobic recovery



INTRODUCTION

Silicones are polymers with a molecular formula of $[R_mSi(O)_{(4-m)/2}]_n$ where $m = 1\text{--}3$ and $n > 1$.¹ Polydimethylsiloxane (PDMS) is the most common type of silicone. Commercially, it is produced by ring opening equilibration polymerization of octamethylcyclotetrasiloxane (D_4) with chain capping molecules as shown in Figure 1.¹ Polymer molecular weight is controlled by x , the molar ratio between D_4 and the chain cappers. Desired end functionality, R , is introduced by chain capping molecules with the appropriate molecular structures. Unavoidably, low molecular weight cyclic siloxanes, D_n , are significant components of the equilibration products. For example, in bulk polymerization, ~ 18 wt % of the products are cyclic siloxanes with D_4 being the most abundant and a continuous population to at least D_{400} .¹ D_4 , D_5 , and D_6 make up >95 wt % of the cyclic siloxane fraction.¹

The ubiquity of silicones in science and technology is attributed to their unique structural characteristics.^{2–4} For example, PDMS is structurally distinct from polymers with

carbon-containing backbones. The Si–O–Si bond angle and the Si–O and Si–C bond lengths are larger and longer than their carbon-based counterparts. The resulting conformational freedom of PDMS chains gives rise to the low glass transition temperature of -123 °C⁵ and the poor mechanical properties of the cross-linked forms. The latter problem is addressed by incorporating significant amounts of silica and other additives in commercial silicone products, such as Dow Corning’s Sylgard-184. Furthermore, even though PDMS is hydrophobic with a low surface tension of ~ 20 mN/m,⁵ the ionic character of the Si–O and Si–C bonds renders PDMS highly water-vapor permeable.⁶ In terms of stability, silicones are more thermally stable than their carbon-based polymer counterparts due to the higher bond strength of Si–O than C–C.⁷ However,

Received: October 16, 2014

Accepted: December 2, 2014

Published: December 15, 2014

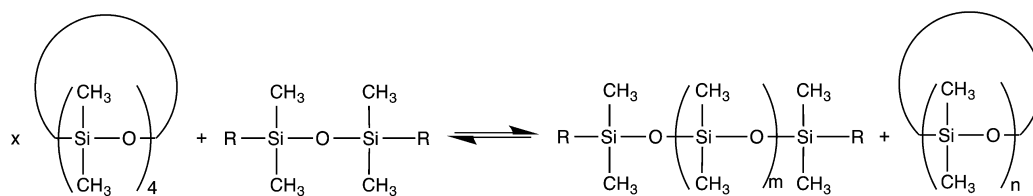


Figure 1. Equilibration polymerization of D_4 where $x = (m + n)/4$.¹

the ionic character of the Si–O bond renders silicones chemically unstable, especially toward bases and acids.

These unique characteristics including elasticity, gas permeability, thermal stability, and reactivity are taken advantage of in many applications.^{3,4} The hydrophobicity exploited for water repellency, however, is not desirable in applications that require the bulk properties of PDMS and hydrophilicity. Thus, significant efforts ranging from plasma treatment to wet chemical approaches have been made to explore methods to hydrophilize PDMS.⁸ Oxygen plasma treatment is the most common method to hydrophilize PDMS substrates because it is fast, benign, and effective. The treatment makes use of a gaseous mixture of high energy species, including electrons, ions, radicals, and excited species to oxidize surface methyl groups.^{9,10} Plasma treatment results in the formation of a silica-like surface layer,^{11–15} SiO_x with each silicon bonded to 3–4 oxygen atoms, making the surface significantly more hydrophilic. Although demonstrably useful, a serious drawback of this approach is that the effect of plasma treatment is temporary, and thus not desirable in long-term applications. PDMS surfaces have been observed to recover their hydrophobicity rapidly, especially within the first few hours after exposure to air,^{16–18} due to the phenomenon known as hydrophobic recovery. The process is spontaneous and is driven by the reduction of the high interfacial energy between the hydrophilic surface and hydrophobic air. Previous studies by Owen and others^{14,19} elucidated the recovery mechanisms to include reorientation of surface hydrophilic groups into the bulk,^{15,20} condensation of surface silanol groups,¹⁵ migration of low molecular weight (LMW) species from the bulk to the surface,^{12,14,20,21} *in situ* generated surface cracks facilitating diffusion of LMW species,^{13,22} and *in situ* created LMW species at the surface.¹⁴ Chromatographic analysis identified extractable species on PDMS surfaces as predominantly small cyclic siloxanes^{20,23} with the *in situ* generated portion being far less than that which migrated from the bulk.²⁰ Among the various mechanisms, surface reconstruction and diffusion of LMW species are dominant when plasma treatment does not cause surface damage and extensive chain scissions. Surface reorientation has been identified as a much faster process than diffusion of LMW species from the bulk to the surface.²⁴ In one study, 1/3 of the total hydrophobic recovery was attributed to surface reorientation while the diffusion of LMW species to the surface was implicated as the major mechanism for the recovery.²⁰ We note that adsorption of organic contaminants from air can also contribute to hydrophobization of hydrophilic silicones. This can be minimized, however, by neutralizing surface charge on plasma-treated samples and storing samples in a clean environment.

Extensive work has been carried out to identify conditions that reduce the rate and extent of hydrophobic recovery. The most notable methods include solvent extraction and optimization of curing, plasma treatment, and post treatment

storage conditions. Solvent extraction takes place prior to surface hydrophilization and involves using a good solvent, such as heptane, to swell the PDMS network to remove the free polymeric/oligomeric species. Extraction of highly cross-linked samples resulted in as much as 5% weight loss.²⁵ This method has been shown to reduce hydrophobic recovery over several days;^{25–27} however, it requires a large amount of organic solvent and is labor and energy intensive.

Curing time and temperature, plasma treatment time and pressure, and post treatment storage conditions also appear to affect the rate and extent of hydrophobic recovery of plasma oxidized PDMS. A brief summary of some recent findings is provided below. Since the existing body of work is vast, the summary is representative, but by no means comprehensive. It should be noted that data from samples treated with gases other than oxygen or later modified with other reagents are not included.

Incomplete cross-linking can increase the rate of hydrophobic recovery, as uncured, free-moving species can migrate easily through an incompletely cross-linked network and adsorb to the hydrophilic surface.²⁶ Due to the codependency of time and temperature, curing conditions vary significantly among different studies. As such, the manufacturer's recommended curing time and curing temperature for Sylgard-184 vary widely, from 35 min at 100 °C to 48 h at room temperature. Curing at low temperature is time-consuming. High curing temperatures increase cross-linking rates and facilitate the evaporation of volatile LMW species and solvent molecules. High temperature conditions, however, may also result in the formation of thermodynamically stable, small cyclic siloxanes, which are reported to occur at temperatures as low as 110 °C.²⁸ Thermal aging at moderate temperature over several days was shown to reduce hydrophobic recovery.²¹ After 14 days of curing at 100 °C, the static contact angle measured after oxygen plasma treatment was 55°.²¹

Oxidation time is also codependent on other plasma conditions, such as power, oxygen pressure, and flow rate, and is typically chosen as the parameter to be optimized. Plasma treatment time varies considerably from 6 s to several minutes and longer. Mild plasma treatment conditions may result in incomplete oxidation of the surface layer. Some studies have shown a correlation between longer plasma treatment time and slower recovery, at least in the first few hours.^{18,29} Extreme plasma conditions have been shown to physically damage PDMS surfaces.^{13,22}

Post treatment storage conditions also affect the rate and extent of hydrophobic recovery. Storage of treated PDMS in a polar environment, such as water, was shown to reduce hydrophobic recovery as compared to storage in air.^{15,17,30} This storage effect was not observed in another study.²⁹ Humidity can also affect the hydrophobic recovery rate, with high humidity resulting in faster recovery than low humidity.¹⁴

Table 1 summarizes the widely varying experimental conditions and the final water contact angles of treated

Table 1. Variety of Experimental Conditions (Material Type, Sample Thickness, Curing Conditions, and Oxygen/Air Plasma Treatment Conditions) and the Corresponding Final Static Contact Angles Reported in Some Previous Studies^a

material, thickness	curing condition	plasma condition	contact angle (deg)	ref
Sylgard-184, 2 mm	24 h, 70 °C	60 s, 2 mTorr	85 ^{ob} after 36 days	25
Sylgard-182, 30 nm	45 min, 100 °C	60 s, 30 W	55° after 14 days	29
Sylgard-184, no thickness info	1 h, 100 °C	60 s, 100 μbar, 20 sccm, 150 W	55° after 13 h	31
Sylgard-184, 2.5 and 5 mm	100 min, 85 °C ^c	12 s, 70 W	55° after 14 days	21
Sylgard-184, 27 μm	24 h, 70 °C	90 s, 100 mTorr, 50W	95° after 3 h	16
Sylgard-184, 1.3 mm	>3 h, 70 °C	120 s, 18 W	65° after 28 days	32
Sylgard-184, no thickness info	2 h, 150 °C	300 s, 70 W	60° after 6 h	18
Sylgard-184, 1.14 mm	1 h, 80 °C	5 min, 18 W	95° after 7.5 days	18
Sylgard-184, 5–10 μm	>12 h, 90 °C	30 s, 200 mTorr, 200 W	85° after 20 days	10

^aSamples were stored in air at room temperature prior to characterization. ^bAdvancing contact angle. ^cFollowed by 14 days of thermal aging at 100 °C.

PDMS from some recent studies mentioned above. It is noteworthy that most of the studies reported only static contact angle, which can be any value between advancing and receding contact angles (θ_A and θ_R). Static contact angles measured a few hours to 20 days after plasma treatment ranged from 50° to 95°. Considering the large contact angle difference between the native hydrophobic PDMS and treated hydrophilic PDMS, the hysteresis (difference between advancing and receding contact angles) or the range of possible static contact angle values on samples during hydrophobic recovery is expected to be significant. The effectiveness in reducing hydrophobic recovery among many studies using drastically different experimental conditions cannot be compared on the basis of static contact angle values alone. Other deficiencies lie in the lack of consistency or control in terms of silicone type, sample thickness, vacuum treatment time prior to plasma oxidation, curing conditions, and plasma treatment conditions.

Sylgard is the silicone of choice in most of these studies even though it contains a significant amount of fillers and additives, which may contribute to hydrophobic recovery. Two other commercially available silicones were included in this study. D^VD^H is a “stripped-down” system prepared from commercially available vinyl-terminated PDMS and poly(hydrido-methylsiloxane) prepolymers. This was chosen to identify the contribution of additives in Sylgard to hydrophobic recovery. The third system, Q^VQ^H, is prepared from two commercially available MQ resins (one containing vinyl-dimethylsilyl groups and the other containing hydridodimethylsilyl groups) and does not contain dimethylsiloxane (D) units. As mentioned earlier, all PDMS samples contain a significant amount of cyclic oligomers, D_n. The removal of these LMW components is the main objective of this and other investigations. If the presence of these LMW species is intrinsic to PDMS systems, silicones without D units should not contain monocyclic oligomers and should be expected to exhibit less hydrophobic recovery after

surface hydrophilization. Sample thickness was not controlled or studied as a variable in the previous studies on hydrophobic recovery. Thickness likely contributes to the hydrophobic recovery of silicone as it determines the “reservoir” depth and migration length for LMW species. There may also be differences in structure between thick and thin film samples. In this study, thick samples were ~1 mm in thickness and were prepared by casting prepolymer mixtures into Petri dishes, while thin samples were a few micrometers in thickness and were fabricated by spin-casting prepolymers on silicon wafers. Comparisons between thin and thick film samples, to the best of our knowledge, have not been carried out previously. We emphasize that oxygen plasma treatment requires evacuation of the reaction chamber prior to plasma ignition, and this subjects samples to reduced pressure, conditions under which volatile LMW species can be extracted. Most prior studies did not comment on this important issue or report the duration of the evacuation process prior to plasma oxidation. In this study, the total vacuum treatment time is precisely controlled as a means to remove LMW species from silicone samples.

Despite the large body of existing studies on hydrophobic recovery of oxygen plasma treated silicones, the deficiencies discussed above are apparent. The present study attempts to fill the voids by identifying key parameters contributing to hydrophobic recovery and establishing protocols for preparing durable, hydrophilic commercial silicones. The efforts were focused on the removal of LMW species via optimizing curing conditions and vacuum treatment time prior to plasma treatment. Both thin (a few μm) and thick (~1 mm) samples were evaluated to identify conditions required to minimize hydrophobic recovery and render long-lasting surface hydrophilicity.

■ EXPERIMENTAL SECTION

Materials. HPLC-grade organic solvents were obtained from Pharmco. Oxygen gas (99.999%) was purchased from Middlesex Gases Technologies. Water was purified using a Millipore Milli-Q Biocel System (Millipore Corp., resistivity ≥18.2 MΩ/cm). Sylgard-184 elastomer kit was purchased from Dow Corning. The following reagents were purchased from Gelest: vinyl-terminated polydimethylsiloxane (D^V, MW = 28 kDa), polymethylhydrosiloxane (D^H, MW = 1.4–2 kDa), octamethylcyclotetrasiloxane (D₄, MW = 297 Da), polydimethylsiloxane trimethylsiloxy terminated (T05 or PDMS⁷⁰⁰, MW = 700–800 Da; T25 or PDMS^{17k}, MW = 15–20 kDa), vinyl-functionalized MQ silicone (Q^V, 0.4–0.6 vinyl equivalent per kg, 50% in xylene), hydride-functionalized MQ silicone (Q^H, 7.8–9.2 hydride equivalent per kg, viscosity 3–5 cP), and platinum-divinyltetramethyldisiloxane complex (Karstedt's catalyst, diluted to 5 × 10⁻⁵ g/mL based on Pt mass in anhydrous toluene). All reagents were used as received without further purification. Silicon wafers (100 orientation, P/B doped, resistivity 1–10 Ω-cm, thickness 475–575 μm) were purchased from International Wafer Service.

Instrumentation. Silicon wafers and PDMS samples were oxidized in a Harrick plasma cleaner PDC-001 (Harrick Scientific Products). Spin-casting was carried out using a Laurell WS-400B-6NPP/LITE single wafer spin processor (Laurell Technologies). Thickness of thin films was measured with a profilometer (Veeco Dektak 150) and by measuring sample mass differences before and after spin-casting. Contact angles were measured using a Ramé-Hart telescopic goniometer with a Gilmont syringe and a 24-gauge flat-tipped needle. Dynamic advancing and receding angles were recorded while the probe fluid, Milli-Q water, was added to and withdrawn from the drop, respectively. Atomic force microscopy images were obtained with an Asylum Research MFP-3D atomic force microscope operated in tapping mode in air.

Three Silicone Systems. For Sylgard samples, a base to curing agent ratio of 10:1 by mass was used. The two components were thoroughly mixed and degassed in vacuum for 30 min to remove bubbles. For $D^V D^H$ and $Q^V Q^H$ samples, vinyl and hydride functionalized prepolymers were mixed at a molar ratio of 1:5 in the presence of ppm level of Pt catalyst. For example, $D^V D^H$ network was prepared using the following procedure. D^V (2.8 g, 0.2 mmol) and 150 μL of 5×10^{-5} g/mL Karstedt's catalyst (3.8×10^{-8} mol Pt or 2.6 ppm Pt based on silicone product mass) were mixed well, followed by the addition of D^H (0.067 g, 1 mmol) and thorough mixing. For thin film preparation, $D^V D^H$ mixture was diluted with 50% toluene to prevent premature cross-linking reaction. Bubbles in $D^V D^H$ and $Q^V Q^H$ samples were either allowed to rise to the top and/or removed by blowing a gentle stream of nitrogen onto the mixture.

Preparation of Thin Films. Silicon wafers were diced into 1.3×1.3 cm² pieces, rinsed thoroughly with distilled water, dried with a compressed air stream, and further dried in a clean oven at 110 °C for 30 min prior to being exposed to oxygen plasma for 15 min at high power (30 W). A 150 μL portion of a prepolymer mixture was dispensed on a clean wafer using a micropipette. Spin-casting was carried out at 6100 rpm for 60 s. Samples were then cured at 100 °C for 1.5 h.

Preparation of Thick Films. Each prepolymer mixture was poured into a clean polypropylene Petri dish of 5 cm in diameter. The amount of the mixture was adjusted so that the final film thickness was ~ 1 mm. The samples were then cured either at 100 °C for 1.5 h or at room temperature for a desired amount of time.

Plasma Oxidation and Hydrophobic Recovery Studies. The plasma sample chamber was evacuated to ~ 100 mTorr, followed by a 30 s oxygen flush at ~ 300 mTorr. The cycle was repeated three additional times. The total amount of time that samples were in vacuum was either 15–25 or 40 min. Plasma treatment was carried out for a desired amount of time at ~ 300 mTorr under high power. Samples were allowed to charge-neutralize in the plasma chamber for 15 min prior to characterization. Dynamic contact angles on treated samples were monitored for at least 30 days. Each reported value is an average of at least eight measurements obtained from at least two samples and four readings from different locations on each sample. The standard deviation of the reported contact angle values is 2° unless indicated otherwise. Samples were stored in a desiccator at room temperature until analysis and were not reused.

Statistical Analyses. Statistical analyses of dynamic contact angles among thin films, among thick films, and between thin and thick films of the same type of material were carried out using *t* tests assuming unequal variances. The values are considered statistically different if the two-tailed *P* values for both advancing and receding contact angles are less than 0.05.

RESULTS AND DISCUSSION

This research was designed on the basis of the established factors contributing to hydrophobic recovery of hydrophilized silicones: surface reorientation of hydrophilic groups to the bulk, condensation of surface silanols, migration of LMW species from the bulk to the surface, and surface cracks and LMW species generated by plasma treatment. Surface crack formation can be readily avoided and generation of LMW species at the surface can be minimized by optimizing plasma treatment time. On the other hand, surface reconstruction, including reorientation of hydrophilic groups and condensation of silanol groups, is driven by surface energy minimization and is therefore unavoidable in hydrophobic materials with glass transition temperatures below room temperature. It is anticipated, however, that the extent of surface reconstruction as measured by increases in dynamic contact angles should be an intrinsic property of a completely cross-linked silicone substrate after being treated with oxygen plasma under optimized conditions. One objective of the research was to

determine the intrinsic contribution of surface reconstruction to hydrophobic recovery. The most challenging aspect of minimizing hydrophobic recovery is to remove LMW species from the silicone systems. D_4 is the main starting material in PDMS manufacture; it is unstrained, and is thus the most thermodynamically stable siloxane.¹ Therefore, the removal of D_4 and other volatile LMW species under reduced pressure and extended curing time was closely examined. Another strategy to eliminate LMW species was to use a silicone system that does not contain D units, which is a new paradigm in minimizing hydrophobic recovery and accomplishing long-term hydrophilicity.

Three Commercial Silicone Systems. Sylgard-184 is the most common silicone used in research and industry. Most surface hydrophilization studies were conducted using Sylgard systems. Due to the poor mechanical properties of PDMS, a significant amount of silica and small molecule additives are in the Sylgard formulation.^{33,34} These additives, if not completely incorporated into the silicone network, can contribute to hydrophobic recovery. In addition to Sylgard-184 (Sylgard), a “stripped-down” cross-linked PDMS ($D^V D^H$) and a methyl-silicone polymer containing no D units ($Q^V Q^H$) were evaluated in this study. All three silicone networks were prepared via hydrosilylation reactions between vinyl groups and Si–H groups in the presence of Karstedt's catalyst as shown in Figure 2. Also shown in the figure are chemical structures of D^V , D^H ,

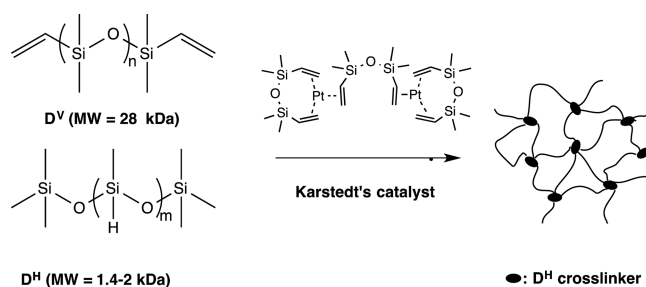


Figure 2. Chemical structures of D^V , D^H , and Karstedt's catalyst; hydrosilylation reaction between vinyl groups in one prepolymer and Si–H groups in another prepolymer results in a cross-linked silicone network.

and the catalyst. Both Q^V and Q^H are highly branched and contain only Q units, $(\text{Si}-\text{O})_4$, that are terminated with vinyl dimethylsilyl and hydridodimethylsilyl groups, respectively. Sylgard-184 was prepared using a 10:1 mass ratio of base agent and cross-linker as recommended by the manufacturer. For $D^V D^H$ and $Q^V Q^H$ systems, a 1:5 molar ratio of vinyl and Si–H groups was used to optimize the mechanical properties of the cross-linked products (results not shown here). Because of the simplicity of the system, $D^V D^H$ was used in the initial optimization studies.

Optimization of Plasma Oxidation Time. To maximize surface hydrophilization and minimize surface damage, plasma treatment conditions were optimized. Due to the codependency of time, pressure, power, and other parameters, plasma treatment time was the only parameter varied while the rest were maintained constant. Dynamic contact angles of $D^V D^H$ thin films after plasma treatment are shown as a function of oxidation time in Figure 3. Untreated $D^V D^H$ films are hydrophobic, exhibiting advancing and receding contact angles of $117 \pm 8^\circ$ and $104 \pm 4^\circ$, respectively. Contact angles decrease rapidly as a function of treatment time until the plateau values

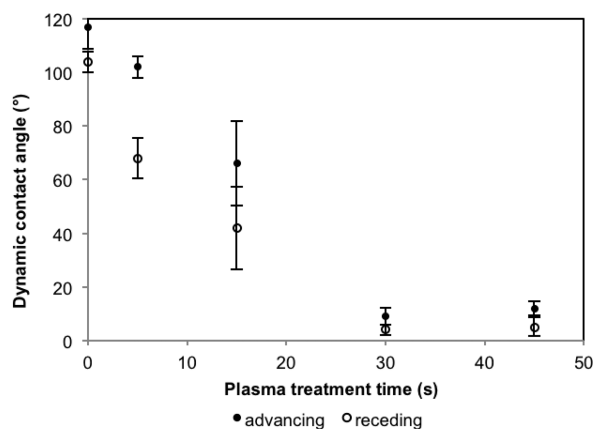


Figure 3. Advancing and receding contact angles of $D^V D^H$ thin films as a function of plasma oxidation time.

of $\theta_A/\theta_R = 10 \pm 3^\circ/5 \pm 3^\circ$ are reached after 30 s of treatment time. Shorter treatment results in not only higher contact angle values but also larger standard deviations, indicating heterogeneous surfaces consisting of both hydrophobic and hydrophilic regions. AFM height images of $D^V D^H$ before and after 30 s plasma treatment (Figure 4) reveal no physical damage from

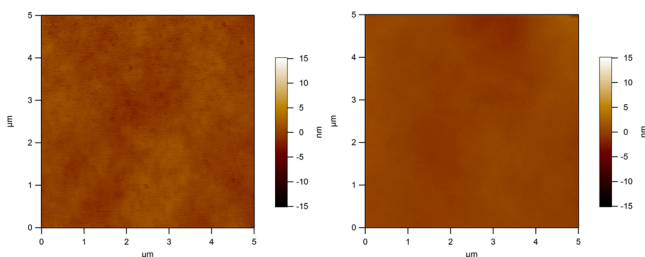


Figure 4. AFM height images (size, $5 \times 5 \mu\text{m}^2$; data scale, 15 nm) of $D^V D^H$ before (left, rms = 0.7 nm) and after (right, rms = 0.5 nm) 30 s of plasma oxidation.

plasma oxidation. Both surfaces appear smooth with root-mean-square (rms) roughness values less than 1 nm. Both phase images are identical and homogeneous (not shown here). Plasma oxidation time of 30 s appears to be the optimal condition to give rise to the lowest contact angles/greatest hydrophilicity achievable without causing visible surface damage on the nanoscopic level.

Oxygen Plasma Treated Thin Films. Hydrophobic recovery studies were extended to more than 30 days to capture the rate and extent of recovery as well as to provide feasibility assessment for long-term applications of hydrophilized silicones. Studies were first carried out on thin films. To assess the contribution of a small amount of additives to hydrophobic recovery, 1 wt % of D_4 , PDMS⁷⁰⁰ (T05), and PDMS^{17k} (T25) were deliberately added to $D^V D^H$ prepolymer mixture prior to curing and plasma oxidation. We note that these samples were subjected to a total vacuum time of 15–25 min prior to plasma treatment. Dynamic contact angles of the plasma treated $D^V D^H$ with and without additives as a function of time are shown in Figure 5. Some features of these plots warrant comment. First, the trends shown by advancing and receding contact angles are almost identical, with the former being consistently $\sim 15^\circ$ higher than the latter. Second, the initial rates of recovery for samples containing the lower molecular weight additives, D_4 and PDMS⁷⁰⁰, are faster than

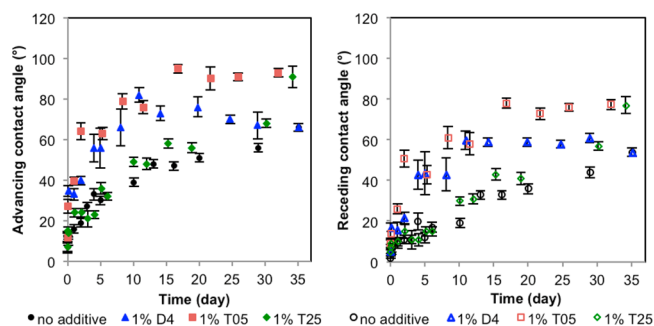


Figure 5. Hydrophobic recovery monitored in terms of advancing and receding contact angles of thin films containing $D^V D^H$ with and without 1 wt % of additives: samples were cured at 100°C for 1.5 h and then evacuated (~ 100 mTorr) for a total of 15–25 min prior to plasma oxidation.

those for samples without additives and with the higher molecular weight (HMW) additive, PDMS^{17k}. This indicates that LMW additives facilitate the hydrophobic recovery. Third, the extents of the recovery as indicated by the contact angle values toward the end of the observation indicate the following trend: PDMS^{17k}, PDMS⁷⁰⁰ > D_4 , $D^V D^H$. The final contact angles for samples containing PDMS⁷⁰⁰ and PDMS^{17k} are similar, $\sim 92^\circ/77^\circ$, even though the initial rates of recovery are very different. We interpret these results with the suggestion that the recovery for samples containing PDMS^{17k} occurs toward the end of the observation due to the slower migration of HMW species to the surface. Fourth, the samples containing D_4 demonstrate unique recovery behavior. The dynamic contact angles rise rapidly to $82^\circ/60^\circ$ within 11 days, but then decline steadily to $66^\circ/54^\circ$, identical to those of $D^V D^H$ without additives.

These initial experiments demonstrate that LMW species (e.g., PDMS⁷⁰⁰) contribute to both the rate and extent of hydrophobic recovery and that HMW species (e.g., PDMS^{17k}) contribute primarily to the extent of recovery. Furthermore, D_4 is volatile and is removed from the silicone substrates under ambient conditions. Hydrophobic recovery can be kept at a minimum if all the functional prepolymers are incorporated into the silicone network and all of the unfunctionalized LMW species, primarily D_4 and other cyclic oligomers, are removed. This led to the decision to extend the total evacuation time to 40 min as an effort to remove as much LMW species as possible. Figure 6 shows the hydrophobic recovery of $D^V D^H$ and Sylgard thin films subjected to a total of 40 min evacuation time prior to plasma oxidation. Both treated $D^V D^H$ and Sylgard thin films exhibit a slow and small extent of hydrophobic recovery. The contact angles rise slightly during the first day as shown in the inset and reached only $51 \pm 2^\circ/38 \pm 2^\circ$ for Sylgard and $56 \pm 2^\circ/39 \pm 2^\circ$ for $D^V D^H$ after 35 days or longer. Considering that the lowest static contact angle reported is 55° after 14 days,^{21,29} our treated thin films exhibit similar if not better hydrophilicity after a much longer period indicating the effectiveness of vacuum treatment prior to plasma oxidation. In comparing the contact angle profiles of $D^V D^H$ thin films shown in Figures 5 and 6 along with results from other thin film samples (not shown here), 40 min vacuum treatment yields slightly better and more consistent results than shorter vacuum treatment for thin film samples.

Oxygen Plasma Treated Thick Films. The same vacuum treatment was applied to Sylgard and $D^V D^H$ thick films, and their hydrophobic recovery profiles are shown in Figure 7. The

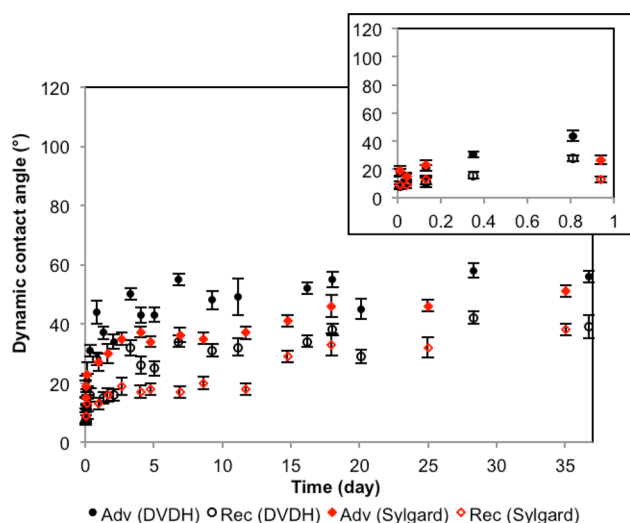


Figure 6. Hydrophobic recovery as monitored in terms of advancing and receding contact angles of Sylgard and $D^V D^H$ thin films: samples were cured at 100 °C for 1.5 h and then evacuated (~ 100 mTorr) for a total of 40 min prior to plasma oxidation. The inset shows that contact angles increase only slightly in the first day.

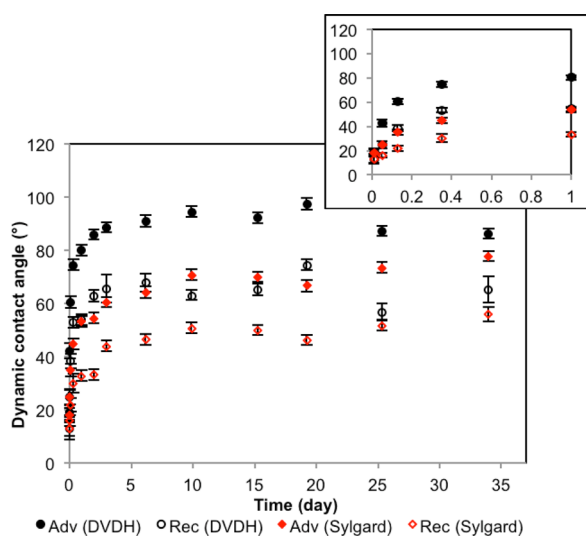


Figure 7. Hydrophobic recovery as monitored in terms of advancing and receding contact angles of thick films: Sylgard and $D^V D^H$ were cured at 100 °C for 1.5 h and then evacuated (~ 100 mTorr) for a total of 40 min prior to plasma oxidation. The inset shows that contact angles increase rapidly in the first day.

rate and extent of recovery are much greater than those of the thin film samples in Figure 6. The dynamic contact angles reached $\theta_A/\theta_R = 86 \pm 5^\circ/65 \pm 4^\circ$ and $78 \pm 2^\circ/56 \pm 3^\circ$ for $D^V D^H$ and Sylgard after more than 30 days, respectively. The obvious explanation is that LMW species deeper in the sample are more difficult to remove under the same experimental conditions.

In principle, longer vacuum treatment of thick films should yield comparable results as thin films, but it could be energy intensive considering that the thick films are 3 orders of magnitude thicker than the thin films. We took a note from the hydrophobic recovery profile of $D^V D^H$ thin films with 1% D_4 added (Figure 5). The decrease in contact angles indicates that D_4 evaporates completely from the silicone matrix at room temperature over time. Kinetics studies of D_4 evaporation in the

pure form and as 10 wt % additives in Sylgard and $D^V D^H$ at room temperature were carried out. The percentage of D_4 mass loss relative to the total amount added over time is depicted in Figure 8. Pure D_4 evaporates completely within 2 days. D_4

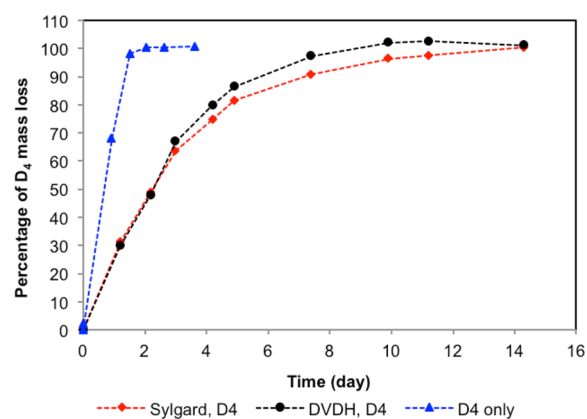


Figure 8. Percentage of D_4 mass loss relative to the total amount in the free form and as 10 wt % additives in Sylgard and $D^V D^H$ thick films as a function of time under ambient conditions.

evaporation from thick silicone films, however, is diffusion limited and takes at least 15 days to complete. D_4 evaporation kinetics indicate that if silicone thick samples are left to cure in open air for 15 days or longer, volatile LMW species, such as D_4 , should have sufficient time to diffuse and evaporate from the substrates. Figure 9 depicts hydrophobic recovery profiles

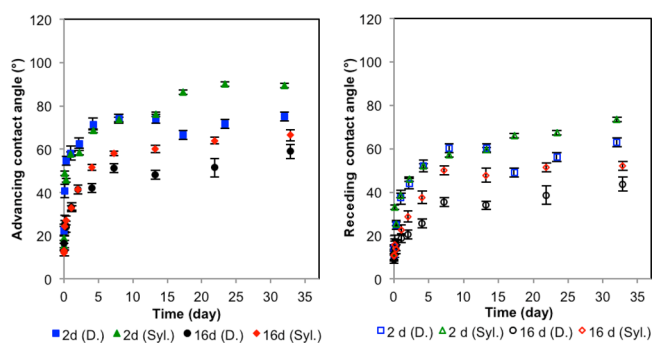


Figure 9. Hydrophobic recovery as monitored in terms of advancing and receding contact angles of thick films: Sylgard and $D^V D^H$ were cured at room temperature for either 2 or 16 days and then evacuated (~ 100 mTorr) for a total of 40 min prior to plasma oxidation.

of Sylgard and $D^V D^H$ thick films that were cured for 2 days and 16 days at room temperature prior to 40 min vacuum treatment and plasma oxidation. The samples that were cured for 2 days showed significant hydrophobic recoveries with contact angles reaching $\theta_A/\theta_R = 89 \pm 2^\circ/73 \pm 3^\circ$ for Sylgard and $75 \pm 2^\circ/63 \pm 2^\circ$ for $D^V D^H$ after more than 30 days. For those cured for 16 days, however, the dynamic contact angles were $\theta_A/\theta_R = 66 \pm 3^\circ/52 \pm 2^\circ$ for Sylgard and $59 \pm 3^\circ/44 \pm 2^\circ$ for $D^V D^H$ thick films after more than 30 days. This is a significant improvement compared to the corresponding thick films cured for 1.5 h at 100 °C (Figure 7).

Silicones without "D". LMW species, especially cyclic oligomers, are hypothesized to be unique to silicones containing D units. $Q^V Q^H$ without D moieties was evaluated as a new silicone system. $Q^V Q^H$ thin films were prepared, cured at 100 °C for 1.5 h, and evacuated for 20 min before 30 s

plasma oxidation. Their dynamic contact angles as a function of time are shown in Figure 10. The hydrophobic recovery of Q^VQ^H thin films is slow and minimal with contact angles reaching $\theta_A/\theta_R = 56 \pm 2^\circ/43 \pm 2^\circ$ after more than 30 days.

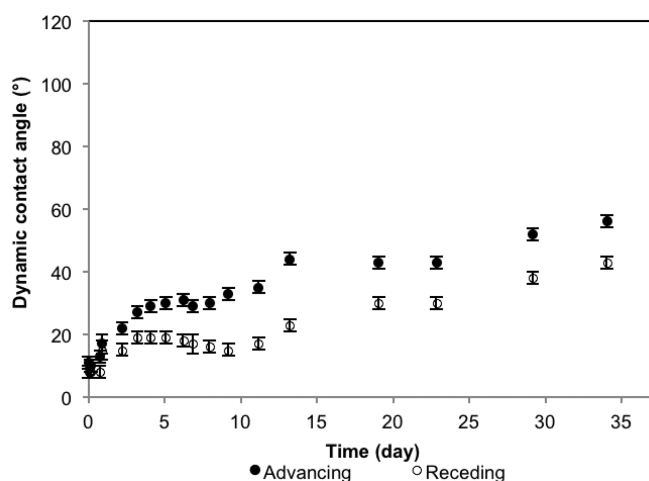


Figure 10. Hydrophobic recovery as monitored in terms of advancing and receding contact angles of Q^VQ^H thin films: samples were cured at 100°C for 1.5 h and then evacuated (~ 100 mTorr) for a total of 20 min prior to plasma oxidation.

The dynamic contact angle data of various oxygen plasma treated silicone samples after more than 30 days are tabulated in Figure 11. A few conclusions can be drawn from the thin film

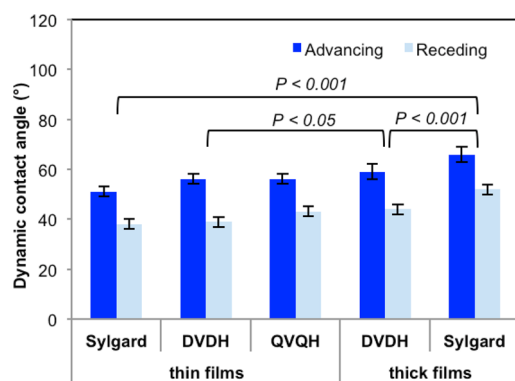


Figure 11. Dynamic contact angles of plasma-oxidized samples under optimized conditions after being stored at room temperature for more than 30 days. The contact angle values between thin and thick samples (Sylgard and D^VD^H) as well as between thick D^VD^H and Sylgard samples are significantly different at the two-tailed P values indicated.

data. First, our plasma treatment yielded more long lasting, hydrophilic silicone thin films than previously reported. Second, vacuum treatment is an effective means to remove LMW species that contribute to hydrophobic recovery from thin films. Third, the difference in the contact angle values of the treated thin films is statistically insignificant implying that surface reconstruction is inherent, contributing to a similar but small increase in hydrophobicity over time. It is also likely that some free, mobile species are too large to be removed under vacuum, but can diffuse slowly to the surface, partially contributing to the observed hydrophobicity.

Figure 11 also includes the lowest contact angles of plasma oxidized Sylgard and D^VD^H thick films after more than 30 days.

These values were obtained on samples cured for 16 days at room temperature and are significantly better than their counterparts cured at 100°C for 1.5 h. The results from thick films are statistically higher than those from the thin films indicating the challenge of removing all of the free, mobile species from a greater sample depth. That the contact angles of thick Sylgard samples are statistically higher than those of D^VD^H samples is attributed to the additives in the former. Attempts to prepare Q^VQ^H thick films failed because xylene, which was used to reduce the viscosity of one of the prepolymers, was difficult to remove and the final films were too brittle to characterize. The comparison between silicone without D units and Sylgard/ D^VD^H thick films cannot be made until more suitable prepolymers are available.

CONCLUSIONS

This is the first study where different silicone systems were evaluated and compared for long-term hydrophilicity after oxygen plasma treatment. In addition to the ubiquitous Sylgard, D^VD^H without additives and Q^VQ^H without D units were chosen to pinpoint the potential contribution of additives and cyclic D_n to hydrophobic recovery. Two strategies were used to minimize hydrophobic recovery of oxygen plasma treated silicone films: modulating plasma oxidation time to maximize hydrophilicity without damaging surface and removing free, mobile species via extended vacuum treatment and room temperature curing prior to plasma oxidation. Dynamic water contact angles were monitored for longer than 30 days after plasma oxidation, and the performances of thin (a few μm) and thick (~ 1 mm) films were compared.

A 30 s oxygen plasma treatment was determined to be the optimal time after which advancing and receding contact angles of the silicone films were drastically reduced from $117 \pm 8^\circ/104 \pm 4^\circ$ to $10 \pm 3^\circ/5 \pm 3^\circ$ without causing any visible surface damage. When 1 wt % additives were incorporated into the thin film samples, hydrophobic recovery was exacerbated. Specifically, LMW additives increased both the rate and extent of recovery while HMW additives primarily increased the extent of recovery. Added D_4 increased the initial rate of the recovery, but did not affect the final recovery due to its volatility. A 40 min vacuum treatment was found to be effective in reducing the hydrophobic recovery of thin film samples by removing LMW species. The final contact angles were $\theta_A/\theta_R = 51\text{--}56^\circ/38\text{--}43^\circ$, and there was no statistical difference among the three types of thin silicone samples. The small and slow rise in contact angle over time is likely caused by surface reorientation of hydrophilic functional groups to the bulk and condensation of surface silanol groups, which are expected to be intrinsic material properties and are unavoidable. Our thin film results are better than what has been previously reported.

Vacuum treatment alone was not as effective for thick samples due to the greater "reservoir" depth and migration length for mobile species. Extensive room temperature curing allows for the evaporation of some LMW species, such as D_4 , and results in reduced hydrophobic recovery. However, the thick films, especially Sylgard samples, exhibit significantly greater hydrophobic recovery than the corresponding thin film samples. This result implies that room temperature curing is not as effective as vacuum treatment in removing larger molecular weight species and that the additives in Sylgard formulation contribute to the inferior performance.

To summarize, removing free, mobile species from silicone thin films under reduced pressure is effective in achieving long-

lasting, superior surface hydrophilicity. Silicone thin films, either free-standing or spun cast on other substrates, are recommended when surface hydrophilization is utilized in long-term applications. The additives in Sylgard contribute to hydrophobic recovery if not removed. Silicones without D, such as Q^VQ^H , are attractive candidates to further explore silicone materials with durable hydrophilicity.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support was provided by the National Science Foundation (DMR-1005324 and DMR-0820506). We thank the Aidala Laboratory at the Physics Department of Mount Holyoke College for AFM access.

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