Colloids and Surfaces A 546 (2018) 186–193

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Strategies to hydrophilize silicones via spontaneous adsorption of poly(vinyl alcohol) from aqueous solution

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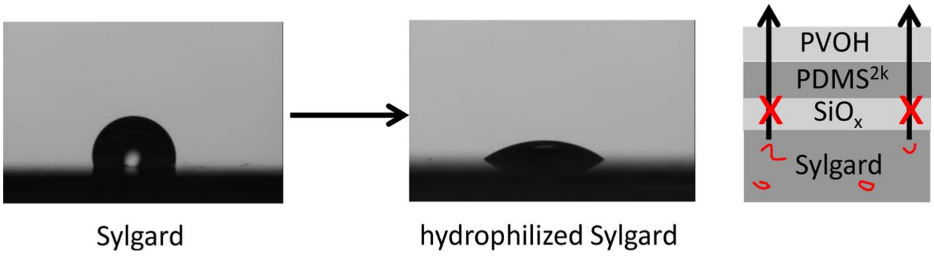
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Hydrophobic recovery
Surface modification
Plasma oxidation
Polymer adsorption
Dewetting
Hydrophilization

ABSTRACT

It is challenging to achieve long-lasting hydrophilicity by surface modification of polydimethylsiloxane (PDMS), principally due to the hydrophobic recovery that occurs. This involves the migration of low molecular weight species from the bulk to the surface and is driven by the reduction of interfacial free energy. In this study, spontaneous adsorption of poly(vinyl alcohol) was carried out on Sylgard PDMS films and their modified derivatives. PDMS^{ox1s}, PDMS^{ox60s}, and PDMS$^{ox60s+2k}$ were prepared by 1-s oxygen plasma, 60-s oxygen plasma, and 60-s oxygen plasma followed by covalent attachment of linear PDMS of 2 kDa molecular weight on PDMS films, respectively. Surface morphology was characterized by optical and atomic force microscopy and hydrophilicity was monitored by dynamic water contact angle measurements. It was found that negligible PVOH adsorption takes place on PDMS^{ox60s} due to the lack of hydrophobic driving force and that extensive PVOH thin film dewetting on PDMS and PDMS^{ox1s} results in insignificant improvement in hydrophilicity. However, a continuous PVOH thin film albeit with some small holes was obtained on PDMS$^{ox60s+2k}$. PDMS$^{ox60s+2k}$-PVOH exhibits advancing and receding contact angles of 80–90°/16 ± 2°, which are significantly lower than 123 ± 5°/97 ± 2° on unmodified PDMS. A range of static contact angles were also measured, some of which are lower than those reported in the literature. The PDMS$^{ox60s+2k}$-PVOH system demonstrates superior long-term and hydrolytic stability, which are attributed to the removal of the driving force for hydrophobic recovery by inserting a hydrophobic PDMS layer between a hydrophilic, plasma-oxidized, PDMS bulk and a hydrophilic PVOH exterior. This is a new concept in addressing hydrophobic recovery of hydrophilized silicones. The spontaneous nature of the adsorption process and the crystallinity of the PVOH barrier layer are the other advantages demonstrated in this study.

1. Introduction

Silicones are widely used in science and technology due to their unique characteristics, such as elasticity, gas permeability, thermal stability, hydrophobicity, and reactivity [1–3]. Polydimethylsiloxane (PDMS) is the most common type of silicone. The hydrophobicity,

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https://doi.org/10.1016/j.colsurfa.2018.03.024
Received 22 December 2017; Received in revised form 27 February 2018; Accepted 8 March 2018

however, causes issues in applications that require adhesion and wetting. Significant efforts ranging from plasma treatment to wet chemical approaches have been made to explore methods to hydrophilize PDMS [4,5]. Oxygen plasma treatment is the most common method to hydrophilize PDMS substrates and makes use of a gaseous mixture of high energy species, including electrons, ions, radicals, and excited species to oxidize surface methyl groups [6,7]. Plasma treatment results in the formation of a silica-like surface layer, SiO_x [8–12].

Hydrophilized PDMS surfaces have been observed to recover their hydrophobicity rapidly, especially within the first few hours after exposure to air [13–15]. Hydrophobic recovery is spontaneous and is driven by the reduction of the high interfacial energy between the hydrophilic surface and air. Owen and others [11,16] attributed the recovery to a number of factors including reorientation of surface hydrophilic groups into the bulk [12,17,18], condensation of surface silanol groups [12], migration of low molecular weight (LMW) species from the bulk to the surface [9,11,17,19,20], *in-situ* generated surface cracks facilitating diffusion of LMW species [10,21], and *in-situ* created LMW species at the surface [11]. The diffusion of LMW species to the surface has been implicated as the major mechanism for the recovery [17]. Solvent extraction to remove free polymeric/oligomeric species prior to surface hydrophilization has been shown to reduce hydrophobic recovery [22–24]. However, this requires a large amount of organic solvent and is labor and energy intensive. We recently reported extraction of LMW species under reduced pressure for thin films and under ambient pressure for thick films prior to oxygen plasma treatment [25]. The method is effective at producing hydrophilized silicone samples that are stable during the monitoring period of 30 days. Despite efforts by us and others to remove existing LMW species, PDMS can undergo equilibration to create LMW species at moderate temperature [26–28]. Therefore, it is inevitable for the newly generated LMW species to migrate to the treated PDMS surface and reduce its hydrophilicity over time.

A potentially effective strategy to retard the migration of existing and newly generated LMW species is to attach a hydrophilic polymer layer to PDMS substrates. This can be accomplished by surface oxidation and grafting of hydrophilic polymers [29–34]. Physisorption of polymers is an attractive alternative due to its spontaneity. More than a decade ago, poly(vinyl alcohol) (PVOH) adsorption from aqueous solution was established as a general method to hydrophilize hydrophobic substrates [35–38]. PVOH is different from other water-soluble synthetic polymers in that it is atactic yet crystalline. The spontaneous PVOH adsorption was attributed to hydrophobic interactions and the subsequent crystallization of PVOH polymer chains at the interface [37]. Earlier attempts at adsorbing PVOH to unmodified PDMS substrates did not yield noticeable change in wettability [39–42]. However, we recently reported significant enhancement in hydrophilicity via PVOH adsorption on silicon-wafer supported covalently attached ^{linear}PDMS of 2 kDa molecular weight (Si-^{linear}PDMS^{2k}) [43]. The substrate is completely covered by a continuous PVOH film of ~3 nm in thickness. As the PDMS molecular weight increases, the adsorbed PVOH thin films dewet on thicker, more liquid-like PDMS layers upon exposure to air. 1-s oxygen plasma treatment of Si-^{linear}PDMS substrates of higher molecular weights generated enough pinning sites to yield more continuous PVOH films [43]. Free LMW species are absent in the attached ^{linear}PDMS layers, therefore, hydrophobic recovery was not a concern. In many applications, however, thick/bulk PDMS substrates require hydrophilization. It is thus important to develop robust methods to address hydrophobic recovery caused by LMW species present in thick PDMS substrates. Trantidou et al. recently reported that stable PVOH films were obtained after depositing 1% PVOH solution onto oxygen plasma treated PDMS substrates and heating the samples to 110 °C for 15 min [44]. Static contact angles of 37 ± 19° and 50–55° were obtained on samples immediately and 30 days after deposition of 99% hydrolyzed PVOH, respectively, indicating some hydrophobic recovery. On the other hand, deposition of 87% hydrolyzed PVOH resulted in stable static contact angles ~25° over the 30-day period [44]. The extent of hydrophilization is difficult to evaluate since dynamic contact angles were not reported.

In this study, spontaneous PVOH adsorption to unmodified and modified Sylgard PDMS films was carried out to determine the conditions under which long-lasting, hydrophilic PDMS can be accomplished. The emphasis was placed on the layered construction of the coating materials to remove the driving force for hydrophobic recovery without requiring the removal of LMW species.

2. Materials and methods

2.1. Materials

Silicon wafers (100 orientation, P/B doped, resistivity 1–10 Ω-cm, thickness 475–575 μm) were purchased from International Wafer Service. Poly(vinyl alcohol) (PVOH: 89–98 kDa and 99 + % hydrolyzed) was purchased from Sigma–Aldrich. Sylgard-184 elastomer kit was purchased from Dow Corning. Polydimethylsiloxane trimethylsiloxy terminated (^{linear}PDMS^{2k}: M.W. = 2 kDa) was purchased from Gelest. HPLC-grade organic solvents were obtained from Pharmco. Oxygen gas (99.999%) was purchased from Middlesex Gases Technologies. All reagents were used as received. Water was purified using a Millipore Milli-Q Biocel System (Millipore Corp., resistivity ≥18.2 MΩ/cm).

2.2. Instrumentation and general methods

Silicon wafers and silicone samples were oxidized (300 mTorr and 30 W) in a Harrick plasma cleaner PDC-001. Samples were kept in the reactor chamber for 15 min to allow charge neutralization prior to removal. Spin coating was carried out using a Laurell WS-400B-6NPP/LITE single wafer spin processor. Contact angles were measured using a Ramé-Hart telescopic goniometer with a Gilmont syringe and a 24-gauge flat-tipped needle. Dynamic advancing (θ_A) and receding (θ_R) angles were captured by a camera and digitally analyzed while Milli-Q water in the syringe was added to and withdrawn from the drop, respectively. The standard deviation of the reported contact angle values is less than or equal to 2° unless specified otherwise. An Olympus BX51 optical microscope in the reflective mode was used to obtain microscopic images of substrates. Nanoscopic surface topography was imaged using a Veeco Metrology Dimension 3100 atomic force microscope (AFM) with a silicon tip operating in tapping mode. Section analyses of surface features were determined using Nanoscope software. There is no delay between reactions other than the required drying time; all the samples were characterized immediately.

2.3. Preparation of silicone samples

Silicon wafers were diced into 1.2 cm × 1.5 cm 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 base-to-curing agent ratio of 10:1 by mass was used for Sylgard samples. The base and toluene (1:1 by mass) were mixed well, followed by the addition of the curing agent and thorough mixing. 150 μL of the mixture was dispensed on a clean wafer using a micropipette. Spin casting was carried out at 6000 rpm for 60 s. Samples were then cured at 100 °C for 90 min.

2.4. Modifications to silicone substrates

Method A: silicone substrates were treated by oxygen plasma for 1 s. Method B: silicone substrates were treated by oxygen plasma for 60 s. Method C: silicone samples were first treated by oxygen plasma for 60 s. 100 μL of ^{linear}PDMS^{2k} polymer was immediately dispensed on each sample using a micropipette. Samples were then heated to 100 °C for 24 h in capped scintillation vials. After the reaction, the samples were rinsed individually with toluene (3 ×), acetone (3 ×), and Milli-Q water (3 ×), and dried under a nitrogen stream to remove excess water and in a desiccator overnight. Each sample was exposed to vacuum (~100 mTorr) for a total of 20 min (normal condition) or 40 min (extraction condition) during the four pump-oxygen flush cycles prior to oxygen plasma treatment.

2.5. Adsorption of PVOH on silicone substrates [43]

A 0.1 wt% PVOH solution was prepared by dissolving 0.1 g of PVOH powder in 100 g of Milli-Q water at 88–94 °C for 3 h under stirring in a clean polypropylene bottle. The PVOH solution was used after equilibration for a few days and within 30 days of preparation. Unmodified and modified silicone substrates were submerged in 15 mL of PVOH solution at room temperature (20 °C) for 24 h. Out of concern that some Langmuir–Blodgett-like deposition might occur when samples were removed through the solution–air interface, the solution was diluted with water a total of six times before removing the samples. For each dilution, 30 mL of Milli-Q water was added to the solution and the mixture was stirred for 1 min, after which 30 mL of solution was removed within 1 min. The samples were dried in a desiccator overnight.

2.6. Hydrophobic recovery and stability studies

Dynamic contact angles on unmodified and treated silicone samples were monitored once a day for 7 days. Each reported value is an average of at least six measurements obtained from at least two samples and three readings from different locations on each sample. Samples were stored in a desiccator until analysis and were not reused. Hydrolytic stability tests were carried out in Milli-Q water for 24 h under ambient conditions.

3. Results and discussion

3.1. PDMS substrates

Sylgard-184, a commercial PDMS-based elastomer, was chosen because it is a widely used material. Here PDMS refers to crosslinked Sylgard PDMS and $^{\text{linear}}$PDMS refers to uncrosslinked linear PDMS. Spin coating was used to prepare smooth PDMS samples of a few microns in thickness so that surface topography can be characterized by AFM and so that samples were thick enough to study the effect of LMW species on hydrophobic recovery. In addition to PDMS control, three modified PDMS substrates – PDMS$^{\text{ox1s}}$, PDMS$^{\text{ox60s}}$, and PDMS$^{\text{ox60s+2k}}$ – were prepared as shown in Scheme 1. Some of the fabrication procedures are adapted from our previous study, where PVOH adsorption takes place on $^{\text{linear}}$PDMS [43]. The fundamental difference is that pre-existing and continuously generated LMW species are absent in $^{\text{linear}}$PDMS but are present in thick PDMS films here. Hydrophobic recovery caused by the LMW species is discussed and addressed in this study.

The rationale for the modification methods chosen is the following: 1-s oxygen plasma treatment on Si-$^{\text{linear}}$PDMS of high molecular weight was effective at minimizing dewetting of the adsorbed PVOH thin films [43]. Here, we judiciously extended the light plasma treatment to thicker PDMS films in method A. Method B involves 60-s oxygen plasma treatment of PDMS films to generate a hydrophilic, silica-like, surface layer. The optimal plasma oxidation time yielding low water contact angles without causing surface damage was determined to be 30 s to 60 s in this study (not shown here), which is similar to the 30-s condition obtained in our previous study where the LMW extraction method was applied [25]. 60 s was chosen to ensure complete surface oxidation in this study. Method C involves covalently attaching $^{\text{linearPDMS2k}}$ to the silica-like PDMS $^{\text{ox60s}}$ surface because continuous PVOH thin films were obtained on Si-$^{\text{linear}}$PDMS^{2k} [43]. Method B also serves as a control for Method C.

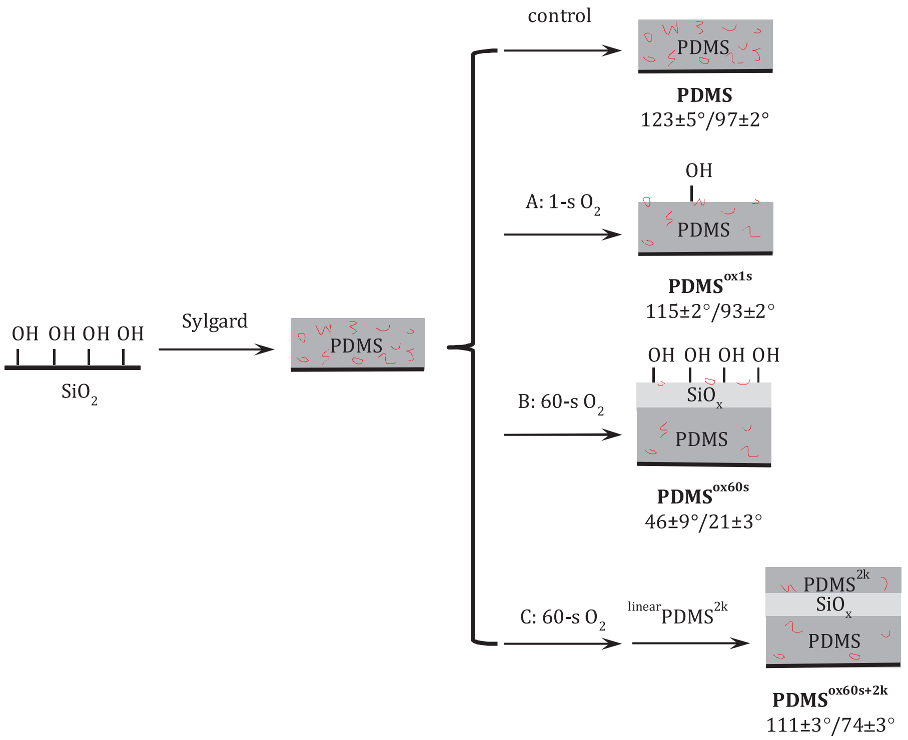
Sylgard PDMS films exhibit advancing and receding water contact angles of 123 ± 5°/97 ± 2° (θ_A/θ_R). The higher than usual hysteresis, the difference between advancing and receding contact angles, is attributed to surface roughness, which will be illustrated in the AFM images later in the section. This result is consistent with the generally accepted effect of surface roughness on dynamic contact angles [45,46]. After 1-s oxygen plasma treatment, both angles were reduced somewhat to 115 ± 2°/93 ± 2° on the PDMS$^{\text{ox1s}}$ substrate. After 60-s oxygen plasma, the hydrophilicity is greatly enhanced to 46 ± 9°/21 ± 2° on the PDMS$^{\text{ox60s}}$ substrate. After the covalent attachment of $^{\text{linear}}$PDMS^{2k}, the contact angles rise to 111 ± 3°/74 ± 3° on PDMS$^{\text{ox60s+2k}}$, which are similar to the values observed on Si-$^{\text{linear}}$PDMS^{2k}, 101 ± 2°/79 ± 3° [43]. This indicates that PDMS$^{\text{ox60s}}$ and silicon wafer have similar reactivity toward $^{\text{linear}}$PDMS^{2k}. Overall the dynamic water contact angle values of the unmodified and modified PDMS thin films qualitatively demonstrate the effectiveness of the modification methods. It is worth noting that contact angles reported here are from samples without extended vacuum extraction of LMW species, thus some hydrophobic recovery has likely taken place after plasma treatment as shown in Scheme 1.

3.2. PVOH adsorption

PVOH adsorption was carried out on the PDMS-based films. The optical micrographs of the samples after adsorption are shown in Fig. 1 (see Fig. S1 for high resolution images). The micron-scale fractal morphologies on the unmodified and 1-s plasma oxidized PDMS are the direct outcome of PVOH thin film dewetting. This is not unexpected and is consistent with the results on Si-$^{\text{linear}}$PDMS of high molecular weights [43]. One main difference is that 1-s plasma oxidation on the much thicker PDMS was not effective at pinning PVOH thin films and preventing them from extensive dewetting. Hydrophobic recovery in the thicker films is responsible for covering (destroying) a significant amount of pinning sites. The features on PDMS$^{\text{ox1s}}$ are somewhat finer than those on the control, which is caused by residual —OH pinning sites. There are no detectable surface features on PDMS$^{\text{ox60s}}$ and PDMS$^{\text{ox60s+2k}}$ by optical microscopy, indicating that either PVOH did not adsorb or that the adsorbed films are smooth on the micron-scale.

Atomic force microscopy was used to probe surface topography on the nanoscopic scale. Fig. 2 shows section analysis of height image, height image, and phase image of PDMS control and PVOH adsorbed on PDMS$^{\text{ox60s}}$ and PDMS$^{\text{ox60s+2k}}$ (see Fig. S2 for high resolution images). PDMS samples prepared by spin coating exhibit “hills” and “valleys” with a length scale in the micron range and a height scale on the nanoscopic level. Silica nanoparticles from the Sylgard formulation are also observed [47,48]. These roughness features contribute to the high contact angle hysteresis mentioned earlier. The PDMS$^{\text{ox60s}}$-PVOH sample appears similar as the PDMS control. The combination of optical and AFM images indicate that there is negligible PVOH adsorption on PDMS$^{\text{ox60s}}$, because of the lack of hydrophobic driving force. On the other hand, the adsorbed PVOH thin film on PDMS$^{\text{ox60s+2k}}$ is mostly continuous with some small holes. The section analysis shows that the holes are ~2 nm in depth, which is comparable to the typical PVOH film thickness of ~3 nm [37,43]. Because of the thinness of the PVOH film and the surface protruding particles, both spinodal decomposition and heterogeneous nucleation can contribute to hole formation. Even though PDMS$^{\text{ox60s+2k}}$ differs from Si-$^{\text{linear}}$PDMS^{2k} in many aspects, both have the silica-$^{\text{linear}}$PDMS^{2k} configuration at the outermost surface. Our results demonstrate that silica-$^{\text{linear}}$PDMS^{2k} surface is an excellent system for supporting continuous PVOH thin films independent of other material composition.

Water contact angles of PDMS$^{\text{ox60s+2k}}$-PVOH are 80–90°/16 ± 2°, which are compared to those of cast PVOH (θ_A/θ_R = 63 ± 2°/17 ± 2°) and Si-$^{\text{linear}}$PDMS^{2k}-PVOH (73 ± 3°/14 ± 2°) films [28,38]. It is reasonable that the receding contact angles are similar because



Scheme 1. PDMS was prepared by spin coating Sylgard-184 on clean silicon wafers. Subsequent oxygen plasma treatment for 1 s yields PDMS^{ox1s} (method A), oxygen plasma treatment for 60 s generates PDMS^{ox60s} (method B), and oxygen plasma treatment for 60 s followed by covalent attachment of ^{linear}PDMS^{2k} produce PDMS$^{ox60s+2k}$ (method C). The relative layer thicknesses are not drawn to scale. The red lines and circles represent LMW species in the PDMS matrices (For interpretation of the references to color in this scheme legend, the reader is referred to the web version of this article.).

receding contact angle measures the wettability of the hydrophilic regions of a heterogeneous surface [49]. That the advancing contact angles increase in the order of cast PVOH film < Si-^{linear}PDMS^{2k}-PVOH < PDMS$^{ox60s+2k}$-PVOH can be attributed to the increasing exposure of PDMS^{2k} in the latter two systems. Holes are apparent in the AFM image of PDMS$^{ox60s+2k}$-PVOH. Even though the AFM image of Si-^{linear}PDMS^{2k}-PVOH does not show obvious holes [43], small holes that are detectable by water molecules must be present [50] to explain its intermediate advancing contact angle. Furthermore, the broader range of advancing contact angles of PDMS$^{ox60s+2k}$-PVOH indicates the heterogeneity of the hole size and distribution in the PVOH films.

3.3. Hydrophobic recovery and stability of hydrophilized PDMS

Dynamic water contact angles were monitored for 7 days after PVOH adsorption to the various PDMS substrates as shown in Fig. 3.

For PDMS and PDMS^{ox1s}, advancing contact angles did not change much but receding contact angles reduced to ~50° after adsorption, consistent with the extensive dewetting of the PVOH films depicted by optical microscopy (Fig. 1). The surface structures after adsorption are stable based on the lack of change in contact angles over time. For PDMS^{ox60s}, the dynamic contact angles are 46°/21° after plasma oxidation (Scheme 1) and ~70°/~30° after PVOH adsorption (day 1 in Fig. 3). After 7 days, the contact angles on PDMS^{ox60s}-PVOH increased to ~100°/~60° (day 7 in Fig. 3). These contact angle data and the micrographs (Figs. 1 and 2) confirm that negligible PVOH adsorption takes place on PDMS^{ox60s} and that hydrophobic recovery of PDMS^{ox60s} is the cause for the contact angle increase from 46°/21° to ~70°/~30°, and to ~100°/~60°. For PDMS$^{ox60s+2k}$-PVOH, dynamic contact angles remained at ~90°/~16° during the 7-day period and 30 days after the sample preparation.

We were surprised by the lack of hydrophobic recovery on PDMS$^{ox60s+2k}$-PVOH because of the holes in the PVOH films (Fig. 2) and the availability of LMW species in the PDMS matrices since extended vacuum treatment was not carried out on these samples. In order for hydrophobic recovery to take place, the LMW species would have to go through the silica layer, the ^{linear}PDMS^{2k} layer, and the PVOH layer or the holes in the PVOH layer. Data presented earlier indicate that LMW species do go through the silica layer on PDMS^{ox60s} causing hydrophobic recovery. The fact that they do not diffuse to the surface of PDMS$^{ox60s+2k}$-PVOH is attributed to the hydrophilic-hydrophobic-hydrophilic three-layer construction on PDMS (PDMS-silica-^{linear}PDMS^{2k}-PVOH) removing the driving force for hydrophobic recovery. The outermost hydrophilic and crystalline PVOH layer further functions as a barrier against the diffusion of the hydrophobic LMW species.

The effect of extended vacuum extraction on the hydrophilicity of PDMS$^{ox60s+2k}$-PVOH was also examined. Fig. 4 compares dynamic contact angles of PDMS$^{ox60s+2k}$-PVOH with and without extended vacuum extraction. The only difference between the two sets of data is that the advancing contact angles of the samples that underwent extended extraction are 5–10° lower. A reason is that the covalent

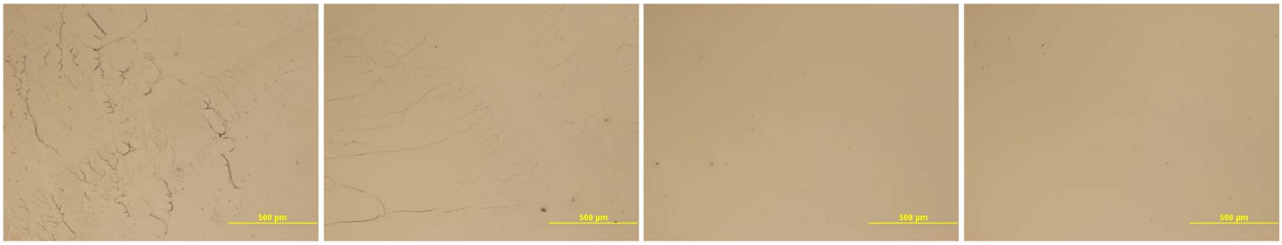


Fig. 1. Optical micrographs (scale bar, 500 μm) of PVOH thin films adsorbed on PDMS, PDMS^{ox1s}, PDMS^{ox60s}, and PDMS$^{ox60s+2k}$ (from left to right).

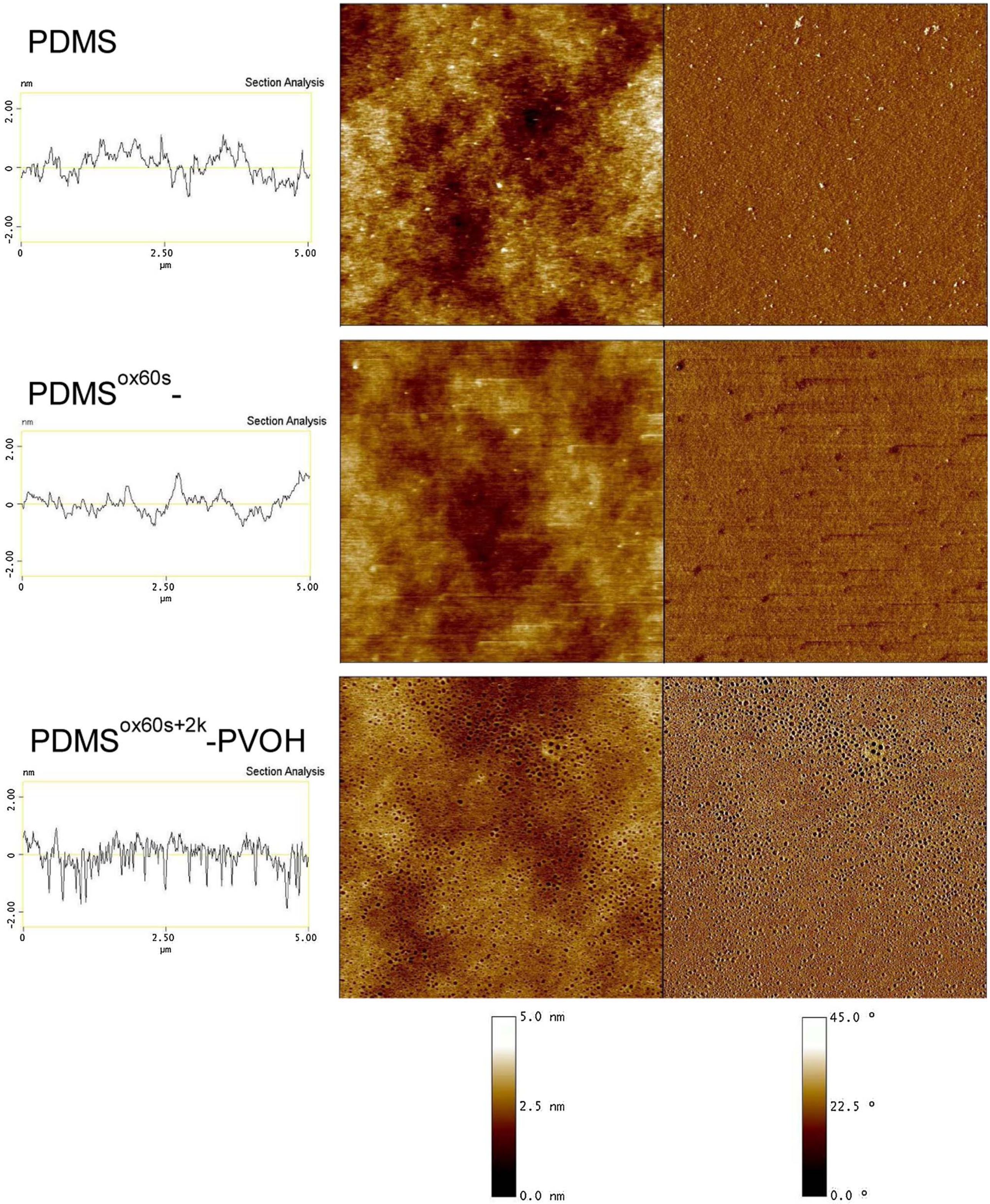


Fig. 2. AFM images (5 μm × 5 μm) of PDMS control, PVOH adsorbed on PDMS^{ox60s}, and PVOH adsorbed on PDMS$^{ox60s+2k}$. For each sample, section analysis, height image (data scale 5 nm) and phase image (phase angle 45°) are shown from left to right.

attachment of ^{linear}PDMS^{2k} is interfered by the LMW species migrated to the silica surface in the system where extended extraction was not carried out (bottom diagram in Scheme 1). However, there is no detectable difference in the adsorbed PVOH film morphology based on optical and AFM images (not shown).

Hydrolytic and long-term stability of the PDMS$^{ox60s+2k}$-PVOH samples were also evaluated. After soaking the samples in Milli-Q water for 24 h, the dynamic contact angles did not change, which is consistent with a previous study [37]. The fibrous features in the PVOH film (Figs. 5, S3 for high resolution images) are similar to those reported in the literature [44], but are very different from the continuous film with small holes before water immersion (Fig. 2). The freshly adsorbed

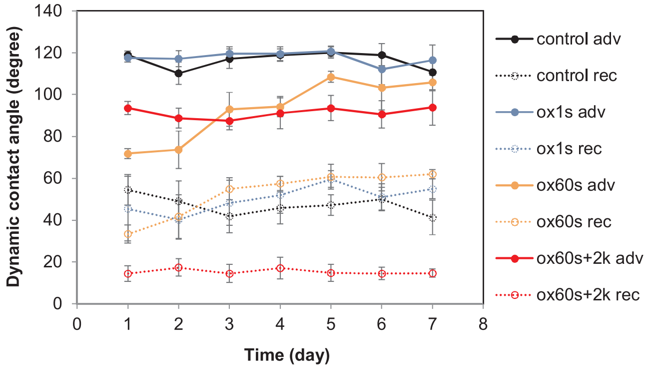


Fig. 3. Hydrophobic recovery monitored in terms of advancing and receding water contact angles on PDMS control, PDMS^{ox1s}, PDMS^{ox60s}, and PDMS$^{ox60s+2k}$ after PVOH adsorption. Advancing and receding contact angles are represented by filled and open circles, respectively.

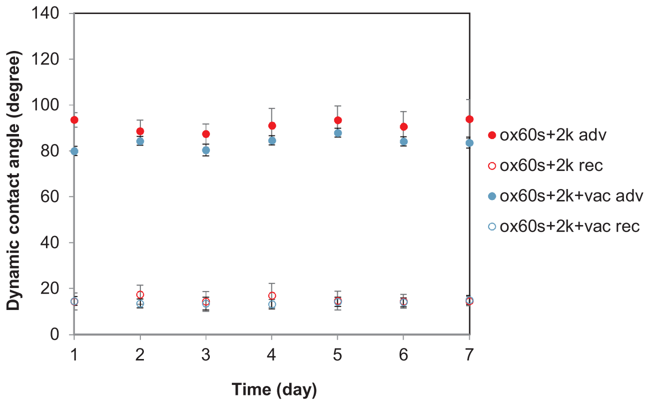


Fig. 4. Hydrophobic recovery monitored in terms of advancing and receding water contact angles on PDMS$^{ox60s+2k}$ after PVOH adsorption. Red and blue symbols represent samples evacuated (~100 mTorr) for a total of 20 min and 40 min, respectively, prior to plasma oxidation (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

PVOH film was allowed to dry in a desiccator and is likely trapped in a non-equilibrium state. On the other hand, the extended water soaking provides a mechanism for PVOH chains to rearrange and crystalize into a more thermodynamically stable thin film. It is worth noting that PVOH thin films, as well as solid PVOH, are not stable at high temperatures, however, lightly crosslinking PVOH with glutaraldehyde renders the adsorbed thin films completely stable at 80 °C without losing their hydrophilicity [37]. Similar strategies can be applied in this system if hydrolytic stability at elevated temperatures is desired. The stability assessment in static water establishes a baseline for aqueous applications under both static and dynamic environments.

The results obtained from this study are compared to those previously reported by us [25] and Trantidou et al. [44] in Table 1. First, the fabrication method used in this study is more complex than the previous ones. In the work by Trantidou et al., PVOH films were deposited, ten times thicker than the ones obtained from spontaneous adsorption [37,43]. Polymer deposition is procedurally simpler than polymer adsorption, but the resulting thin films may not be as reproducible and stable. Second, our dynamic contact angles remained similar, 91 ± 6°/15 ± 4° (normal condition) and 86 ± 4°/16 ± 2° (extraction condition), after the 30-day period on PDMS$^{ox60s+2k}$ adsorbed with 99% hydrolyzed PVOH. The advancing contact angle is higher and the receding contact angle is lower after 30 days in this study than in the previous studies. Only static contact angles were reported by Trantidou et al. [44]. For comparison purposes, static contact angles were measured on PDMS$^{ox60s+2k}$-PVOH after 30 days. Fig. 6 shows images of three static drops with contact angle values of 62°, 43°, and 36°. These data illustrate that static contact angle can assume any value between advancing and receding contact angles depending on the method of deposition and the interaction time between the drop and the substrate. Because dynamic contact angles were not reported in their paper, it is difficult to compare the results. Third, hydrophobic recovery was observed in both previous studies but not in this study (Fig. 4). Overall each method has its distinct advantages. The two previous studies used straightforward fabrication methods yielding PDMS substrates with low water contact angles and good stability. In comparison, the fabrication method applied in this study is more complex generating modified PDMS substrates with higher advancing angles and lower receding angles. The contribution of this study is the demonstration of a new strategy to completely remove the driving force for hydrophobic recovery caused by pre-existing or newly generated LMW species in PDMS bulk migrating to the outermost surfaces.

4. Conclusions

PVOH adsorption was carried out on unmodified and modified Sylgard PDMS films to enhance wetting. On PDMS control and 1-s oxygen plasma oxidized PDMS, adsorption resulted in extensive PVOH dewetting hence insignificant improvement in hydrophilicity. On 60-s oxygen plasma treated PDMS, negligible adsorption took place due to the lack of hydrophobic driving force. On the other hand, covalent attachment of linear 2 kDa PDMS polymer to 60-s oxygen plasma treated PDMS resulted in a system that supports spontaneous PVOH adsorption and continuous PVOH thin film formation. Advancing and receding contact angles decreased from 123 ± 5°/97 ± 2° on PDMS to 80–90°/16 ± 2° on PDMS$^{ox60s+2k}$-PVOH. The hydrophilized PDMS exhibits a range of static contact angles, some of which are lower than those reported in the literature. PDMS$^{ox60s+2k}$-PVOH is stable during a 30-day period and after soaking in water for 24 h. The robustness of our method lies in the removal of the driving force for hydrophobic recovery via the three-layer construction of silica-PDMS^{2k}-PVOH on

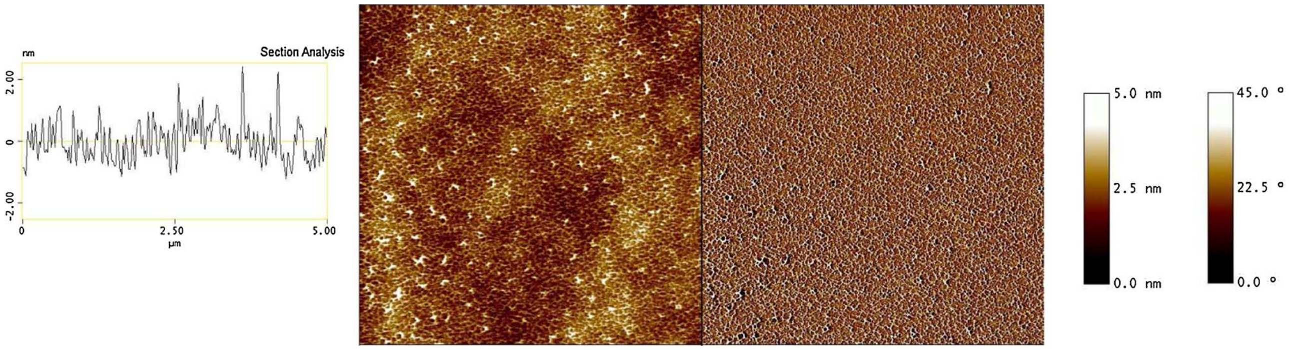


Fig. 5. AFM images (5 μm × 5 μm) of PDMS$^{ox60s+2k}$-PVOH after soaking in Milli-Q water for 24 h at 20 °C. Section analysis, height image (data scale 5 nm) and phase image (phase angle 45°) are shown from left to right.

Table 1
Comparison between this study and two relevant previous studies [25,44].

	Methods	Water contact angles after 30 days	Hydrophobic recovery	Advantage
This study	-PDMS oxidation -linear PDMS attachment -PVOH adsorption	$\theta_A/\theta_R = 80-90^\circ/16 \pm 2^\circ$	No recovery	Removing driving force for recovery
Ref. [25]	-LMW extraction -PDMS oxidation	$\theta_A/\theta_R = 51-56^\circ/38-43^\circ$	Some recovery	Relatively simple
Ref. [44]	-PDMS oxidation -PVOH deposition -heating	$\theta_s = \sim 25^\circ; 50-55^\circ$	Some recovery	Relatively simple

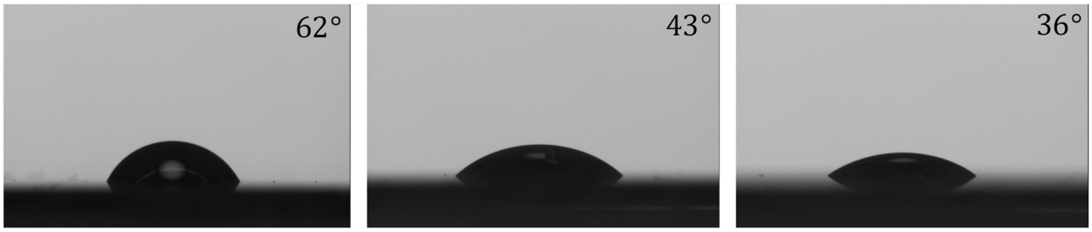


Fig. 6. Images of static drops with their contact angle values on 30-day old PDMS$^{ox60s+2k}$-PVOH with dynamic contact angles of 80–90°/16 ± 2°.

PDMS so that the existing and newly generated LMW species in PDMS matrices do not cause any adverse effect. This study demonstrates a new concept in addressing hydrophobic recovery. The spontaneity of PVOH adsorption as well as the hydrophilicity and crystallinity of the PVOH polymer provide additional advantages in our approach.

Acknowledgements

Financial support was provided by the National Science Foundation (DMR-1404668) and Mount Holyoke College. The authors are grateful to Dr. Alexander Ribbe for his assistance with the AFM work.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.colsurfa.2018.03.024.

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