

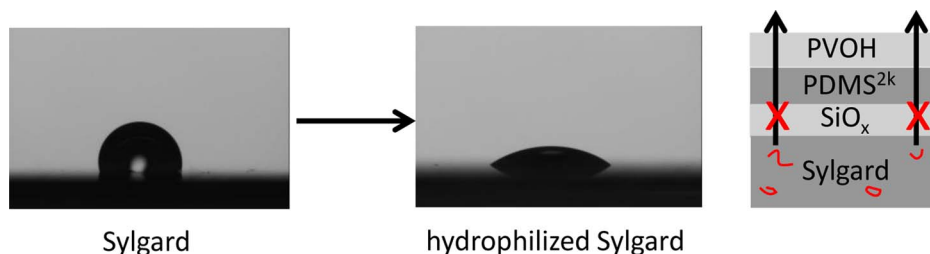
Strategies to hydrophilize silicones via spontaneous adsorption of poly(vinyl alcohol) from aqueous solution



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GRAPHICAL ABSTRACT



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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. $\text{PDMS}^{\text{ox}1\text{s}}$, $\text{PDMS}^{\text{ox}60\text{s}}$, and $\text{PDMS}^{\text{ox}60\text{s}+2\text{k}}$ 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 $\text{PDMS}^{\text{ox}60\text{s}}$ due to the lack of hydrophobic driving force and that extensive PVOH thin film dewetting on PDMS and $\text{PDMS}^{\text{ox}1\text{s}}$ results in insignificant improvement in hydrophilicity. However, a continuous PVOH thin film albeit with some small holes was obtained on $\text{PDMS}^{\text{ox}60\text{s}+2\text{k}}$. $\text{PDMS}^{\text{ox}60\text{s}+2\text{k}}$ -PVOH exhibits advancing and receding contact angles of $80\text{--}90^\circ/16 \pm 2^\circ$, which are significantly lower than $123 \pm 5^\circ/97 \pm 2^\circ$ on unmodified PDMS. A range of static contact angles were also measured, some of which are lower than those reported in the literature. The $\text{PDMS}^{\text{ox}60\text{s}+2\text{k}}$ -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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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 $\text{Si}^{\text{linear}}\text{PDMS}^{2k}$ [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 $\text{Si}^{\text{linear}}\text{PDMS}$ substrates of higher molecular weights generated enough pinning sites to yield more continuous PVOH films [43]. Free LMW species are absent in the attached $\text{Si}^{\text{linear}}\text{PDMS}$ 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 $37 \pm 19^\circ$ and $50\text{--}55^\circ$ 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 $\sim 25^\circ$ 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 $\Omega\text{-cm}$, 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 ($\text{Si}^{\text{linear}}\text{PDMS}^{2k}$; 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 $\text{M}\Omega/\text{cm}$).

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 \times 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 $\text{Si}^{\text{linear}}\text{PDMS}^{2k}$ polymer was immediately dispensed on each

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