FACILE METHODS TO MAKE PDMS HYDROPHILIC: A TIME EVOLUTION STUDY FOR MICROFLUIDIC DEVICES

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ABSTRACT

Flexible microfluidics have found extensive utility in the biological and biomedical fields. A leading substrate material for compliant devices is polydimethylsiloxane (PDMS). Despite its many advantages, PDMS is inherently hydrophobic, limiting its use in passive (pumpless) microfluidics. To this end, many physical and chemical modifications to PDMS have been introduced, ranging from amphiphilic molecule additions to surface plasma treatments. When transitioning from lab benchtop to realized medical devices, these modifications must exhibit long-term stability. We have investigated an array of PDMS modifications, utilizing contact angle goniometry to study surface energy over a 30-day evolution study. Samples were stored in air and water, and Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) analysis was used to confirm surface functional group uniformity. We have identified preferred modification techniques for long-lasting PDMS devices and characterized often overlooked material stability.

KEYWORDS

Microfluidics, Polydimethylsiloxane, Contact Angle, Hydrophilization

INTRODUCTION

Emerging technological advances have pushed the boundaries of microfluidics with regard to a diversity of biotechnology applications, especially in the area of bioMEMS and personalized health monitoring [1]. For compliant wearable devices, stability, flexibility, and a tunable level of elasticity are of particular importance [2]. To this end, polymers have been employed with success. A forerunner material has long been polydimethylsiloxane (PDMS), a polymerized silicone rubber employed for its flexibility, optical transparency, easy fabrication, low cost, tunable mechanical properties, and biocompatibility [3].

Despite these many upsides, PDMS has an inherently low surface energy thereby rendering it a hydrophobic material, which is a significant issue in microfluidic applications when passive, pumpless flow is desired. Much work has been done to resolve this issue [4]. These strategies include plasma treatment surface activation, polymer grafting, surfactant additions, wet chemical treatments, and UV/ozone treatments. Each approach relies on a different method of effectively introducing silanol, carbonyl or other polar functional groups on the surface of PDMS micro-channels. Many, however, are plagued by rapid hydrophobic recovery due to molecular rearrangement in the PDMS polymer network. Consequently, stable device fabrication for application specific microfluidics is reliant on the proper material and/or treatment choice.

Our project involves the design of a microfluidic device for biomarker sensing in passively sampled interstitial fluid (ISF) [5]. As a complex device with multiple manufacturing steps, simplicity in fabrication is key. Accordingly, we have studied the long-term stability of multiple, simple PDMS modifications, as well as understanding the mechanisms that lead to their hydrophilic nature through FTIR-ATR and atomic force microscopy (AFM), These modifications include the addition of surfactants to the PDMS prepolymer mixture, substrate roughening for micro-structuring of the PDMS surface, extraction of low molecular weight oligomers, nano-structuring of the PDMS surface via reactive ion etch (RIE) plasmas, and polymer grafting. Contact angles were measured for increasing time increments over a 30-day storage period in either an air or water ambient for each treatment type.

EXPERIMENTAL METHODS

Chemicals and Materials

The following materials were used as received: Sylgard 184 silicone elastomer (Dow Corning), 4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol (Triton X-100) (Sigma), Polyethylene glycol sorbitan (Tween 20) (Sigma), Pluronic F-127 (Sigma), 2-hydroxyethyl methacrylate 99+% (HEMA) (Sigma), sodium dodecyl sulfate 99+% (SDS) (Sigma), Poly(dimethylsiloxane-b-ethylene oxide) 25:75 (PDMS-b-PEO) (Polysciences), polyalkyleneoxide modified heptamethyltrisiloxane /allyloxypolyethyleneglycol methyl ether (Silwet L-77) (Fisher), xylenes (Fisher), acetone (Fisher), toluene (Fisher), ethanol (Warner Graham), and low density polyethylene (LDPE) petri dishes.

Sample Fabrication

Six distinct chemical modifications, described in subsequent sections, were investigated alongside pristine, unmodified Sylgard 184 PDMS to characterize their hydrophilic behavior. Samples were cured in an oven at 65 °C for 4 hours.

Surfactants

Selected surfactants were added to the PDMS prepolymer mixture before curing. These amphiphilic molecules hydrophilize PDMS by molecular rearrangement of polar groups to the surface upon introduction of water. Chosen surfactants and concentrations are listed in Table 1. Static contact angles of DI water on surfaces were measured over time.

Table 1: Surfactants and respective concentrations (w/w) added to PDMS for molecular hydrophilization.

Surfactants & Concentrations				
Silwet L-77	**Triton X-100**	**Tween 20**	**PDMS-b-PEO**	**Pluronic F-127 (200 mg/mL EtOH)**
0.2 %	1%	1%	0.5%	2 μL/g PDMS
0.4 %	2%	2%	1.0 %	6 μL/g PDMS
0.6 %	3%	3%	1.5 %	10 μL/g PDMS

Extracted PDMS Oxidation

An early method for fabricating long-term hydrophilic samples, introduced by the Whitesides group [6], relies on the extraction of low molecular weight oligomers from the bulk of a cured PDMS substrate. This technique was adapted using three pairs of consecutive solvent soaks (each repeated 1x): 1 hr in 200 mL xylenes, 1 hr in 200 mL toluene, and 1 hr in 200 mL acetone. After 4 hr drying at 65 °C, surfaces were treated with O_2 plasma at 100 W for 30s. Contact angles were measured over time.

Substrate-mediated Micro-roughening

Zhang et al. recently developed a method of roughening PDMS microfluidic channels for the purpose of isolating and recovering circulating tumor cells [7]. In adapting this method, LDPE petri dishes were etched in 1:1 Acetone:EtOH without stirring for 150 and 300 s, after which, a pre-mixed PDMS batch was poured into the dishes. After degassing and curing, the samples were peeled from the etched dishes and treated with O_2 plasma at 100 W for 30 s. Contact angles were measured over time and RMS surface roughness was measured using AFM.

RIE Surface Nano-structuring

Select pristine, cured PDMS surfaces were structured with ion plasmas, adapted from literature [8,9], using an Oxford PlasmaLab 80 with recipes outlined in Table 2. One structuring method employed a single plasma etch step (recipes 1-2), while another utilized two (recipes 3-4).

Table 2: RIE recipes for nanostructure etching and silanolization of PDMS surfaces.

	Step	Gas	Flow [sccm]	Time [min]	Press. [mTorr]	Power [W]
1	1	O_2	20	15	75	150
2	1	O_2	20	30	75	150
3	1	SF_6	60	5	30	600 (ICP)
	2	O_2	20	1	100	100
4	1	SF_6	60	10	30	600 (ICP)
	2	O_2	20	1	100	100

Polymer Grafting

Select pristine PDMS samples were modified via surface grafting of HEMA. After curing, the surfaces were treated with O_2 plasma for 30 s at 100 W. Subsequently, ~0.5 mL HEMA was spin-coated at 1500 rpm for 15 s, then a second plasma treatment for either 150 s or 300 s was conducted. HEMA hydrophilization may be attributed to monomeric carbonyl groups polarizing PDMS surfaces [9].

Contact Angle Measurements

Images of DI water droplets on each surface were recorded using a Basler acA2500-60um camera with a 6X close focus zoom lens (Edmund). Images were analyzed using ImageJ to extract static contact angles (SCA). Specifically, "contact_angle.jar" was used for circle fitting to contact angles < 20° and "DropSnake" was used for active contour polynomial fitting to contact angles > 20°. This has been illustrated in Figure 1 (a) and (b).

Surface Topographical Characterization

Both pristine and roughened PDMS surfaces were characterized using an NTEGRA Prima AFM. Images of size 5 x 5 μm and resolution 512 x 512 pixel were obtained using tapping mode, then analyzed to compare respective RMS roughness values.

FTIR-ATR Analysis

In order to determine the surface functional groups, a selection of samples were analyzed using a Varian 3100 FTIR/ATR spectroscopy system.

RESULTS & ANALYSIS

Surfactants

When amphiphilic materials are added to a PDMS mixture, water introduced on the surface promotes molecular rearrangement of polar groups to the surface, increasing sample hydrophilicity. The kinetics of the transforming contact angle can be described by the Ward-Tordai equation (Eq. 1), which describes the time-dependent surface excess concentration ($\boldsymbol{c_s}$) of surfactant,

$$c_s(t) = 2c_0\sqrt{Dt/\pi}-2\sqrt{D/\pi}\int_0^{\sqrt{t}} c_{ss}\,d(\sqrt{t-\tau}) \qquad (1)$$

where $\boldsymbol{c_0}$ is the bulk surfactant concentration, $\boldsymbol{D}$ is the effective bulk diffusion coefficient, and $\boldsymbol{c_{ss}}$ is the subsurface concentration [10]. Assuming an inverse proportionality between surface concentration and contact angle, one can derive relative surface concentration and diffusion constants from SCA measurements. Static contact angle measurements of a droplet on a PDMS-b-PEO modified sample presented in Figure 1(c) displays this effect.

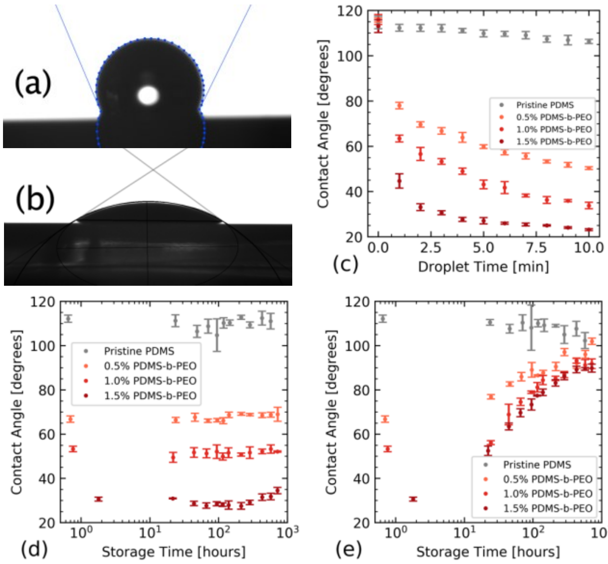

Figure 1: Images of water droplets on pristine (a) and hydrophilized (b) PDMS surfaces. Hydrophilicity increases over time when water sits on the surface of a surfactant-added sample (c). Contact angle is stable over time for air storage (d) but when stored in water, hydrophilicity drops over time as surfactant molecules deplete into the aqueous environment (e).

However, when considering device shelf-life, especially in the context of commercializing a microfluidic medical product, long-term stability becomes a critical parameter. Figures 1(d-e) illustrate how contact angles vary over a timescale of 30 days for three PDMS-b-PEO concentrations in addition to pristine PDMS.

Extracted PDMS Oxidation

Extraction of non-crosslinked oligomers from the bulk deters molecular rearrangement of surface functional groups. This allows for extended hydrophilic stability of plasma-introduced hydroxyl surface groups for samples stored in air. Conversely, extracted samples showed insignificant improvement over non-extracted plasma-treated PDMS samples when stored in water, as polar interaction with the aqueous environment remained dominant on the surface and consequently, molecular rearrangement was unfavorable.

RIE Surface Nano-structuring

In the case of homogeneous wetting (Wenzel state), surface roughness correlates with the roughness ratio, *r*, as

$$\cos(\boldsymbol{\theta_m}) = \boldsymbol{r}\cos(\boldsymbol{\theta_Y}) \qquad (2)$$

where $\boldsymbol{\theta_m}$ is the measured SCA and $\boldsymbol{\theta_Y}$ is the Young CA. Stable surface roughness can be generated through anisotropic reactive ion etching. As has been demonstrated by the Gogolides group, SF_6 anisotropically etches nanocolumns into PDMS surfaces [8]. Whereas O_2 plasma etched samples saw negligible change in roughness for doubled etch time from 15 to 30 mins, SF_6 plasma etched samples saw a 190% increase in RMS roughness for doubled etch time from 5 to 10 mins. These differences correlated with wettability and hydrophobic recovery, as long-etch SF_6 samples had delayed recovery timescale and lower final contact angle than shorter etched, whereas insignificant change was demonstrated by increased O_2 etch time.

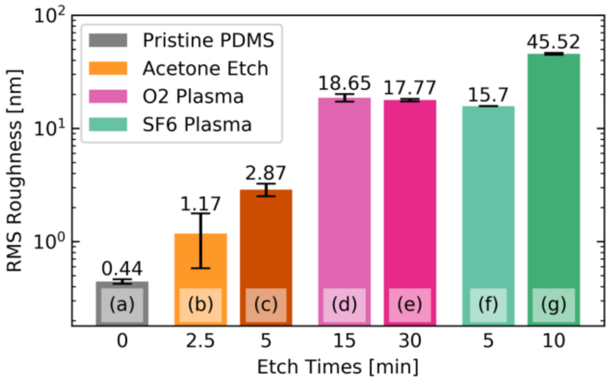

Figure 2: RMS roughness values measured by AFM for three types of etching when compared with pristine PDMS (a): acetone micro-roughening of substrate (b-c), O_2 (d-e) and SF_6 (f-g) anisotropic ion etching.

Substrate-Mediated Micro-roughening

Wet etching of petri dishes for PDMS molding allowed for micro-roughening of the PDMS surfaces. After subsequent plasma treatment, samples demonstrated negligible delay in hydrophobic recovery as compared to standard plasma treated samples, as both 150s and 300s etched samples recovered to a hydrophobic state within 8 days.

Polymer Grafting

Grafting of HEMA onto PDMS surfaces delayed and impeded hydrophobic recovery, with increasing effectiveness for longer plasma treatment times. This process introduces a more permanent hydrophilic state, but still displays recovery patterns characteristic of PDMS. FTIR-ATR spectral analysis confirms HEMA presence on the PDMS surface.

Table 3: Initial and final contact angles from select sample surfaces. (- = not recorded)

Modification Process	**Static Contact Angles [degrees]**		
	Initial θ	**Final θ (Air)**	**Final θ (Water)**
PEO 0.5%	66.8	68.9	101.9
PEO 1%	53.3	52.1	91.8
PEO 1.5%	30.6	34.5	89.8
Silwet 0.6%	65.1	70.6	93.4
Triton 3%	76.0	78.3	85.1
O_2 Plasma	9.8	102.7	29.3
Extracted	9.0	60.8	33.9
O_2 15 min	13.0	107.2	-
SF_6 10 min	23.4	83.1	-
HEMA 300s	18.8	88.1	-
Acetone 300s	16.0	87.5	-

FTIR-ATR Results and Analysis

Representative PDMS surfaces were examined with FTIR-ATR and resulting spectra are presented in Figure 3(a). So as to identify functional group changes introduced by modifications, a pristine PDMS spectrum was subtracted from each modified PDMS spectrum to yield Figure 3(b).

The HEMA grafted spectrum yielded many relevant differences from pristine PDMS. The absorption bands around 3450, 2938, and 1725 cm^{-1} are representative of monomeric HEMA -OH, $-CH_2$, and C=O groups. The downward peaks at 2961, 2905, 1257, 1015, and 792 cm^{-1} represent reductions in symmetric and asymmetric CH_3 stretch, Si-O-Si deformation, and $Si\text{-}(CH_3)_x$ concentrations. The PDMS-b-PEO added sample displayed reductions in 1057 and 755 cm^{-1} peaks, relating to Si-O-Si (shoulder) and $Si\text{-}(CH_3)_2$ excitations. O_2 plasma-treated PDMS displayed an increase in the 1015 cm^{-1} Si-O-Si peak. Finally, SF_6-roughened and subsequently O_2-oxidized PDMS displayed reduced 2960, 2903, 1257, 1007, and 788 cm^{-1} peaks, indicating a decrease in symmetric and asymmetric CH_3, Si-O-Si, and $Si\text{-}(CH_3)_x$ stretches. Bands around 1025 (SiF_4), 907 (SiF_2), 840 (SiF), and 805 cm^{-1} may indicate Si-F bonds left behind by SF_6 plasma bombarding [11,12]. No further investigations are undertaken in this work to identify Si-F bonding, and some peaks appear shifted due to nearby reduction in bands such as 788 cm^{-1} $Si\text{-}(CH_3)_2$, and vice versa. Additionally, the sharp Si-OH peak in the ~3750 cm^{-1} region is not visible as it is orders of magnitude smaller in intensity compared with the recorded spectrum [9].

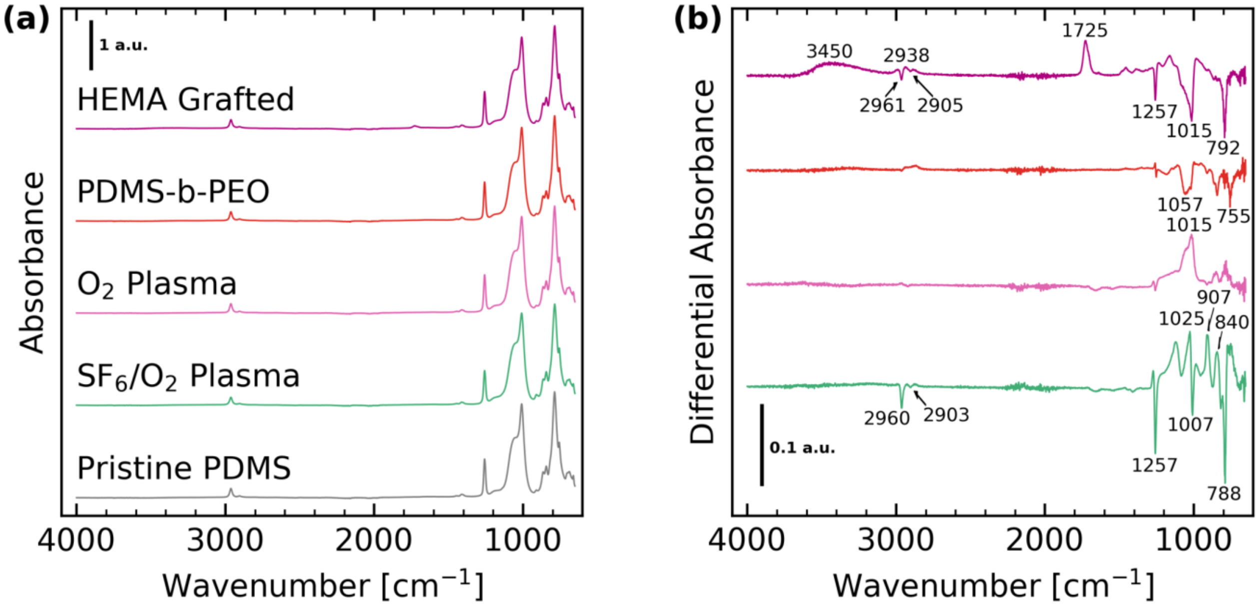

Figure 3: (a) FTIR-ATR spectra of five PDMS samples (bottom to top): unmodified, SF_6 nanoroughened then oxidized, O_2 plasma oxidized, PDMS-b-PEO added, and HEMA-grafted PDMS. (b) Absorbance difference between modified samples and unmodified PDMS. Significant peaks are labeled by wavenumber and discussed in the text.

CONCLUSION

Microfluidic device functionality relies on either active pumping or capillary action of the enclosed fluid owing to hydrophilic materials. PDMS has found much success in medical device construction due to its low cost and characteristic properties, but is intrinsically hydrophobic. To reconcile its hydrophobicity with microfluidic application, many methods of surface hydrophilization have been formulated. We studied the hydrophobic recovery of an array of modifications, utilizing surface contact angles to characterize surface energy, and FTIR-ATR and AFM to characterize the surface properties. Addition of amphiphilic surfactants to the PDMS mixture yielded stable samples for air storage over 30 days, however, molecules were depleted over time in water storage, and require contact time for molecular rearrangement for polar groups to the surface to prompt hydrophilicity. Low molecular weight oligomer extraction using high-swelling solvents delayed and inhibited hydrophobic recovery by preventing molecular rearrangement of O_2 plasma induced silanol groups on the surface. Multiple roughening techniques demonstrated the utility of increased surface roughness on hydrophilic nature after silanolization. A PDMS-b-PEO surfactant additive was identified as the optimal modification for long-term device stability in air storage.

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