

LONG-LASTING SUPERHYDROPHILIC PDMS SURFACE BY ATMOSPHERIC-PRESSURE PLASMA POLYMERIZATION

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ABSTRACT

In this study, a method to modify hydrophobic PDMS (Polydimethylsiloxane) surface to be long-lasting hydrophilic surface by applying atmospheric-pressure plasma polymerization is proposed. To enhance the sustainability of the modified hydrophilic PDMS, two kinds of plasma polymerized layers were implemented on the surface of the PDMS block sequentially. The highly cross-linked hydrocarbon layer deposited by atmospheric-pressure plasma polymerization from CH₄ plays a role as a physical barrier layer (PBL) to prevent hydrophobic recovery of the hydrophilic layer deposited from TEOS (Tetraethylorthosilicate) and O₂. The modified PDMS surface shows long-lasting superhydrophilic wetting property over 28 days of aging time.

KEYWORDS: Polydimethylsiloxane (PDMS), Surface Modification, Atmospheric-pressure Plasma Polymerization

INTRODUCTION

Polydimethylsiloxane (PDMS) is widely used for the microfabrication of various lab-on-a-chip devices because it is inexpensive, biocompatible, self-sealable, and highly elastic; further, it has excellent optical transparency and allows for easy device fabrication. However, the innate hydrophobicity of PDMS causes non-specific binding of biomolecules by physical adsorption, limits to utilize PDMS in electric-osmotic flow applications, and requires external mechanical or electrical power source to generate liquid transport in microfluidics [1]. To overcome the innate hydrophobicity of PDMS, the surface modification of the PDMS surface to hydrophilic might be a solution utilizing gas-phase processing or wet chemical methods [2]. Since gas-phase processing requires vacuum condition and wet chemical methods need complex protocols, those are cost inefficient as well as time consuming. In addition, those methods showed rapid hydrophobic recovery of the modified PDMS surface. The proposed method in this study provides not only several benefits including fast simple fabrication procedure, unlimited substrate size and parallel processing by applying atmospheric-pressure plasma polymerization [3] but also long-lasting superhydrophilic PDMS surface by coating two heterogeneous layers consecutively.

EXPERIMENTAL

Sylgard 184 PDMS prepolymer and cross-linking agent were mixed at the ratio of 10:1 by mass and stirred. Then, the mixture was poured into 4" polystyrene Petri dishes to form a 1-mm-thick layer, degassed in a vacuum desiccator for removing bubbles, and cured in an oven at 80 °C for 90 min. Subsequently, the flat PDMS samples were cut into 2 cm × 4 cm pieces and peeled off the dishes.

For depositing thin film layers, an atmospheric-pressure plasma polymerization system operating at a radio frequency (RF) of 13.56 MHz was utilized. Ultra-high-purity Helium was used as the carrier gas; CH₄ or TEOS vapors were used as the reactant for the PBL deposition, while a mixture of TEOS vapors and O₂ was used for depositing the hydrophilic SiO_x layer on the PBL. An RF power of 200 W was employed for plasma deposition. The distance between the nozzle head of the plasma source and the sample was adjusted to 1.5 mm for PBL deposition and 2 mm for the hydrophilic layer deposition.

The optimal processing condition utilizing the heterogeneous-double-layer deposition was investigated by monitoring the static contact angle on the seventh day following surface modification representing the rate of hydrophobic recovery of the modified surface. A design of experiment (DOE) was performed to identify the optimal processing conditions using a standard L₁₈ orthogonal array. The main effects of the factors were evaluated based on a general liner model analysis of variance (ANOVA).

To compare the long-term hydrophilicity after surface modification, four PDMS samples— unmodified PDMS sample, PDMS modified by single-layer deposition using CH₄ (CH₄/PDMS), PDMS

Table 1. Factors considered in the DOE study of heterogeneous-double-layer deposition for long-lasting hydrophilic PDMS surface

Factor			Level		
			1	2	3
Processing conditions for the PBL	A	Reactant	CH ₄	TEOS	-
	B	No. of head movements	30	60	90
Processing conditions for the hydrophilic layer	C	O ₂ flow rate	100	150	200
	D	He flow rate	5	10	15
	E	No. of head movements	30	60	90

by single-layer deposition using TEOS-O₂ (TEOS-O₂/PDMS), and PDMS modified by heterogeneous-double-layer deposition (TEOS-O₂/CH₄/PDMS)— were prepared.

To validate the optimal conditions and investigate the effect of hydrophobic recovery during the aging time, static contact angle of each sample were measured on 0, 7, 14, and 28 days after surface modification. To analyze the long-lasting hydrophilicity of heterogeneous-double-layer (TEOS-O₂/CH₄/PDMS), the modified PDMS surfaces were characterized by using static contact angle measurement, XPS analysis and SEM images comparing with single layer PDMS without PBL (TEOS-O₂/PDMS) deposited by atmospheric-pressure plasma polymerization using TEOS-O₂ only.

RESULTS AND DISCUSSION

To investigate the optimal processing condition for heterogeneous-double-layer, five factors and their levels for L₁₈ orthogonal array were selected among the processing parameters as shown in Table 1. Based on the L₁₈ orthogonal array, each sample with 18 processing conditions was prepared and the static contact angle was measured after 7 days to monitor the influence of the hydrophobic recovery of the modified PDMS surface (Table 2). Table 3a shows the ANOVA for the whole runs and Table 3b for the half runs only (Factor A: CH₄). The optimal processing condition A₁-B₃-C₂-D₁-E₃ for the long-lasting hydrophilic surface can be determined.

Table 2. Processing conditions with L₁₈ orthogonal array and static contact angle measured on 7 days after surface modification

Run	Factor					Static C.A. (°)
	A	B (No.)	C (sccm)	D (slm)	E (No.)	
1	CH ₄	30	100	5	30	18.6
2	CH ₄	30	150	10	60	17.7
3	CH ₄	30	200	15	90	21.3
4	CH ₄	60	100	5	60	14.0
5	CH ₄	60	150	10	90	19.8
6	CH ₄	60	200	15	30	54.2
7	CH ₄	90	100	10	30	22.5
8	CH ₄	90	150	15	60	17.1
9	CH ₄	90	200	5	90	5.5
10	TEOS	30	100	15	90	146.8
11	TEOS	30	150	5	30	61.0
12	TEOS	30	200	10	60	42.9
13	TEOS	60	100	10	90	147.6
14	TEOS	60	150	15	30	89.9
15	TEOS	60	200	5	60	17.5
16	TEOS	90	100	15	60	138.7
17	TEOS	90	150	5	90	154.4
18	TEOS	90	200	10	30	116.6

Table 3. Main effects in DOE study of static contact angles by ANOVA for (a) full runs in L₁₈, (b) half runs from Run 1 to Run 9 (Factor A: CH₄)

	(a) ANOVA for full runs in L ₁₈					(b) ANOVA for half runs Factor A: CH ₄ (Run 1 to Run 9)			
	A	B	C	D	E	B	C	D	E
Level 1	21.18	51.38	81.37	45.17	60.45	19.18	18.37	12.70	31.77
Level 2	101.70	57.16	59.97	61.17	41.31	29.33	18.18	20.00	16.25
Level 3	-	75.78	42.98	77.97	82.56	15.02	26.98	30.83	15.52
Variance	29177.2	976.1	101.0	344.5	547.2	162.7	48.5	52.9	200.6
Contribution	77.8%	2.6%	5.9%	4.3%	6.8%	35.0%	10.4%	11.4%	43.2%

Figure 1 shows that static contact angle of TEOS-O₂/CH₄/PDMS maintained to be superhydrophilic during 28 days of aging time. On the other hands, that of TEOS-O₂/PDMS increased drastically from 0° to about 113° over the aging time. The O/Si ratio increased abruptly in the TEOS-O₂/CH₄/PDMS samples, and the O/C ratio in the TEOS-O₂/PDMS and TEOS-O₂/CH₄/PDMS samples increased (Table 4(a)). Refinement of the C 1s and Si 2p peaks in the XPS spectra revealed that these elements existed in two different chemical states. These observations confirmed that the hydrophilicity of the modified PDMS surface was obtained by the incorporation of oxygen-containing groups on the surface. The silicone-silicate ratio on the PDMS surface reversed after surface modification by atmospheric-pressure plasma polymerization with TEOS-O₂ (TEOS-O₂/PDMS and TEOS-O₂/CH₄/PDMS): the silicate content became four times higher than the silicone content as shown in Table 4(b). Because of the negative electrical polarity of the chemical bonds, the silicate group is more hydrophilic than silicone, and hence, a silicate-rich surface would be highly hydrophilic. Thus, silicate-silicone ratio is the major factor determining the surface hydrophilicity of PDMS modified by atmospheric-pressure plasma polymerization using TEOS-O₂.

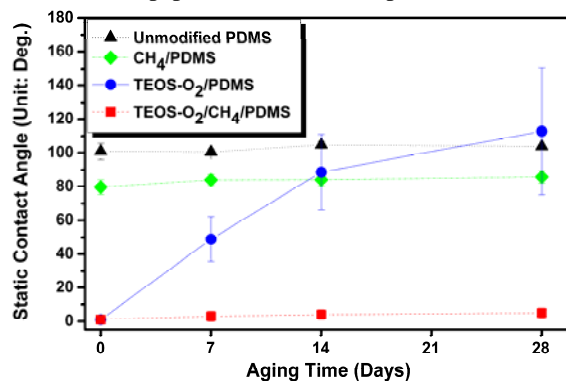


Figure 1: Static contact angle measured 0, 7, 14, and 28 days after surface modification

Table 4. Surface chemical compositions and relative percentages of bonds to XPS C 1s peaks and Si 2p peaks for unmodified and modified PDMS surfaces

	(a) Chemical composition (at. %)					(b) Chemical bonds (area %)			
	C	O	Si	O/Si	O/C	C 1s peaks		Si 2p peaks	
						-C-C-	-C-O-	Silicone	Silicate
Unmodified PDMS	44.92	27.17	27.91	0.97	0.60	95.5%	4.5%	72%	28%
CH ₄ /PDMS	57.28	22.60	20.12	1.12	0.39	92.3%	7.7%	71%	29%
TEOS-O ₂ /PDMS	23.43	44.81	31.76	1.41	1.91	84.9%	15.1%	18%	82%
TEOS-O ₂ /CH ₄ /PDMS	29.50	61.50	9.00	6.83	2.08	91.9%	8.1%	18%	82%

Figure 2 shows surface morphology analysis of TEOS-O₂/CH₄/PDMS showed that the initial SiO_x layer has been conserved over the aging time, while that of TEOS-O₂/PDMS without the PBL showed that the SiO_x layer degrades steadily by the diffusion of PDMS molecules resulting in the loss of hydrophilicity. The monitoring of static contact angle of the modified surfaces corresponded to the surface morphology analysis.

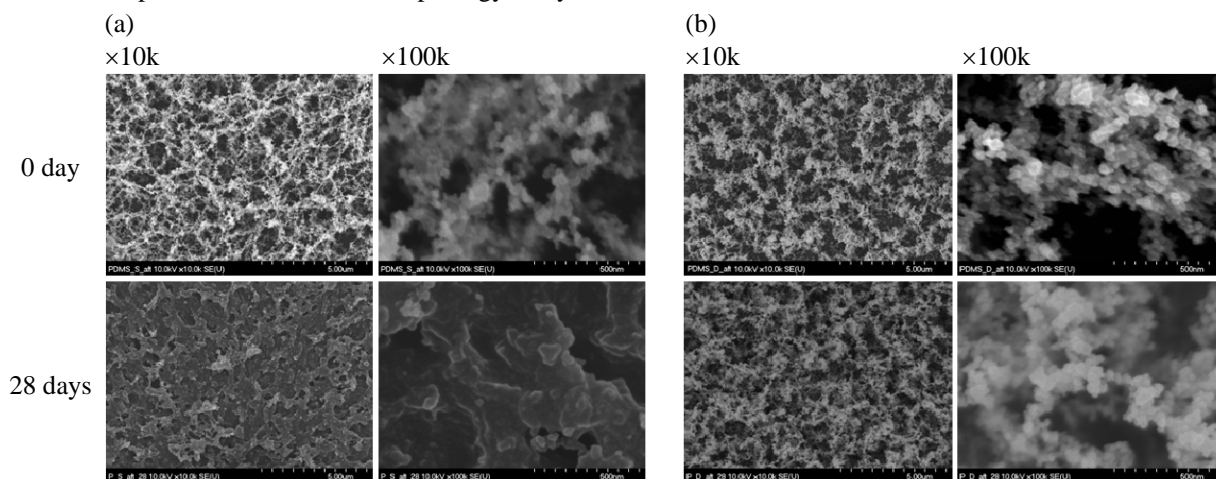


Figure 2: Variation in surface morphology on the day of surface modification (0 day) and 28 days of aging (a) TEOS-O₂/PDMS with $\times 10k$, $\times 100k$ magnification, (b) TEOS-O₂/CH₄/PDMS with $\times 10k$, $\times 100k$ magnification

CONCLUSION

In this study, the deposition of the heterogeneous-double-layer on PDMS (TEOS-O₂/CH₄/PDMS) by atmospheric-pressure plasma polymerization was proposed for long-lasting hydrophilic surface modification of PDMS. Utilizing the DOE study, the optimal processing condition was determined. The modified PDMS surfaces were analyzed by using static contact angle, XPS analysis, and SEM images and characterized focusing on the long-lasting hydrophilicity and the functionality of PBL. It is believed that the atmospheric-pressure plasma polymerization of the heterogeneous-double-layer (TEOS-O₂/CH₄) on PDMS is promising to the cases where long-lasting hydrophilic wettability of innately hydrophobic materials is required.

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