

Investigation on Coating Methods of a Self-Assembled Monolayer on PDMS (Poly (dimethylsiloxane)) Surface

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Abstract

This paper examines PDMS surface treatment methods that can be applied to immobilize a hydrophilic polymer membrane in a PDMS microchannel by covalent bonding. After creating -OH groups on a PDMS surface by UV/ozone treatment, we form SAM on the surface using 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) or 3-(trichlorosilyl)propyl methacrylate (TPM) reagent. Contact angles between a water droplet and SAM-coated PDMS surfaces decreased due to -OH groups generated on the surfaces. The surface functionalized with TMSPMA resulted in the smallest contact angle of 46°. Raman spectroscopy showed that the intensities of Raman shifts were strongest for the surface functionalized with TMSPMA. Overall, functionalizing a PDMS surface with TMAPMA resulted best among the methods examined in this study.

Keywords: SAM, PDMS, Functionalization, Contact angle

Introduction

On-chip sample pretreatment is a critical functionality to automate biochemical analyses using a Lab-on-a-Chip. The on-chip sample pretreatment includes a sample preconcentration process that amplifies the concentration of nascent target molecules to increase detectivity, a mixing process that enhances mixing of two or more fluids at a low Reynolds number, a purification process that extracts or separates target molecules from a complex solution, and so on¹⁻³. The use of polymer structures fabricated in microchannels is one of effective methods to develop on-chip sample pretreatment techniques. Nanoporous polymer membranes were in-situ fabricated in microchannels using

a laser-polymerization technique to develop a microdialysis system and an electrophoretic sample preconcentrator^{4,5}. A chip-based electro-chromatography technique was also developed by photo-patterning a polymer monolith in a microchannel⁶.

The substrate materials of a microfluidic chip are either glass (fused silica, quartz, and etc) or plastics (PDMS, PMMA, and etc). A glass chip is transparent for ultraviolet (UV), chemically stable, heat-resistible, and easy to modify the surface properties. However, it is difficult to accurately control microchannel dimensions during the wet-etching process of chip fabrications due to the isotropic feature of the wet-etching. In addition, the glass chip fabrication is relatively expensive because it requires a hard-lithography. On the other hand, PDMS chips are widely used because they have superior bio-compatibilities and optical properties. Also, a soft-lithography used for a PDMS chip enables the routine fabrications of high quality micro or nano structures at a low cost. However, the hydrophobicity of PDMS due to -CH₃ groups on the surface often makes it difficult to fabricate and immobilize hydrophilic polymer structures in PDMS chips^{7,8}.

In order to modify the surface properties of PDMS to be hydrophilic, various techniques have been utilized. Among the techniques, UV grafting or UV/ozone treatment methods are frequently employed⁸⁻¹¹. Unfortunately, these techniques could result in the deformation of a PDMS substrate or could change the transparent properties of PDMS since they aim at modifying the surface properties of a PDMS substrate. For a hydrophilic polymer structures fabricated in a PDMS microchannel to covalently bond on the channel wall, it is suggested to coat a UV-treated microchannel with a self-assembled monolayer (SAM) which does not alter the optical properties of PDMS^{12,13}.

This paper examines PDMS surface treatment methods that can be applied to immobilize a hydrophilic polymer membrane in a PDMS microchannel by covalent bonding. After creating -OH groups on a PDMS surface by UV/ozone treatment, we form SAM on the surface using two different functionalization reagents. We describe the details of surface treatment procedures, and discuss the results of functionalized surface properties and structures using contact angle measurements and RAMAS spectroscopy.

Functionalization of PDMS Surfaces

In order to form SAM on the PDMS surfaces with -OH groups, we functionalized the surfaces with two reagents, TMSPMA and TPM shown in Figure 1, in the following three different methods. First, deionized water is mixed with 0.4% (v/v) TMSPMA and 0.4% (v/v) acetic acid. TMSPMA is hydrolyzed in an acidic condition, and reacts with -OH groups^{12,13}. A PDMS specimen with -OH groups is immersed in the

TMSPMA mixture for 3 hours, and is rinsed thoroughly with 1-propyl alcohol and deionized water. Second, perfluorooctane and TPM are mixed at a ratio of 1 g to 20 μ g. A PDMS specimen with -OH groups is immersed in the mixture for three hours, and is cleaned with perfluorooctane and ethanol¹⁴. Third, heptane is mixed with carbon tetrachloride at 4 : 1 (v/v). TPM is diluted to 1 mM with this mixture. Then, a PDMS specimen with -OH groups is placed in the 1 mM TPM mixture for one hour¹⁵, and is rinsed with hexane and deionized water.

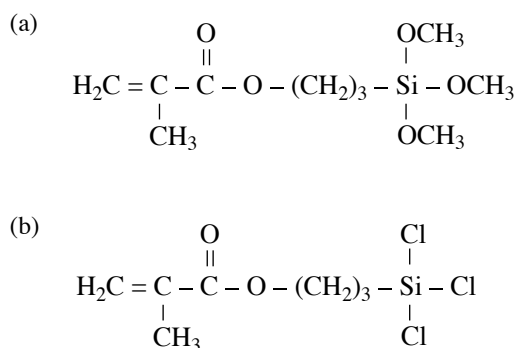


Figure 1. Chemical structure of (a) 3-(trimethoxy-silyl) propyl methacrylate (TMSPMA) and (b) 3-(trichlorosilyl) propyl methacrylate (TPM).

Results

Contact Angle

A contact angle between a water droplet and the surface of a PDMS specimen was measured using a digital image as shown in Figure 2. The contact angle between a droplet and the untreated surface of a specimen (Figure 2a) was about 99°, indicating that the surface was hydrophobic. A PDMS surface functionalized with TMSPMA exhibited a contact angle of about 46° (Figure 2b), implying that the surface became hydrophilic. The mixture of perfluorooctane and TPM led to a contact angle of 71° (Figure 2c)

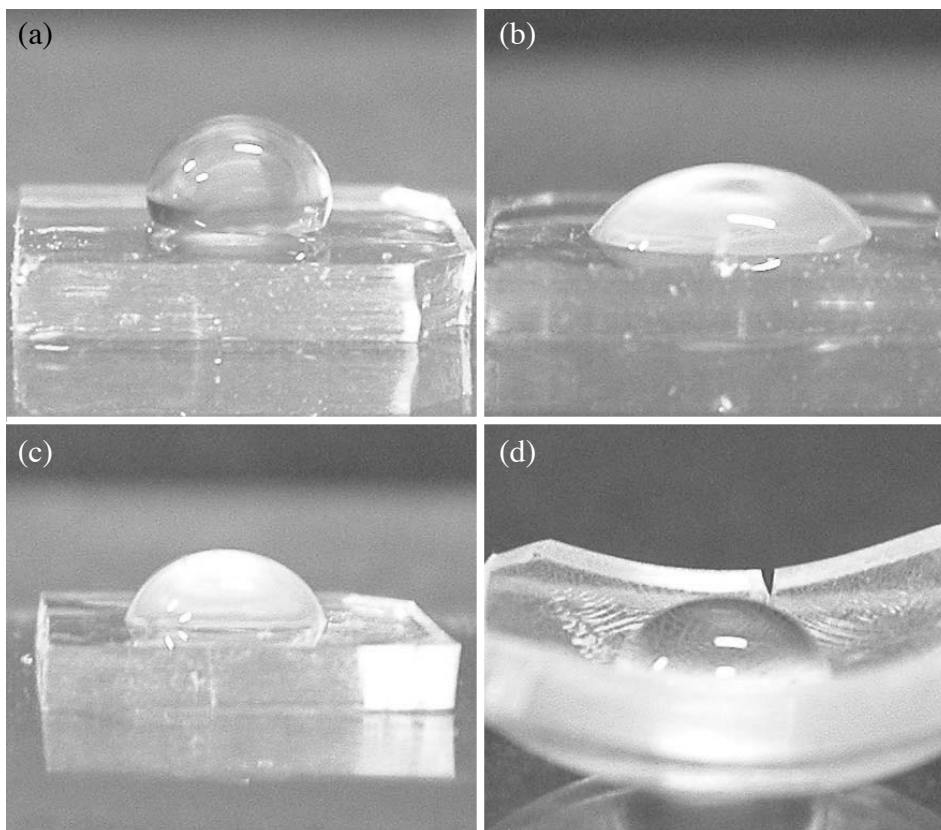


Figure 2. Contact angle measurements using a water droplet on (a) untreated surface, (b) surface functionalized with TMSPMA, (c) surface functionalized in the mixture of perfluorooctane, and TPM (d) surface functionalized in the mixture of heptane, carbon tetrachloride, and TPM.

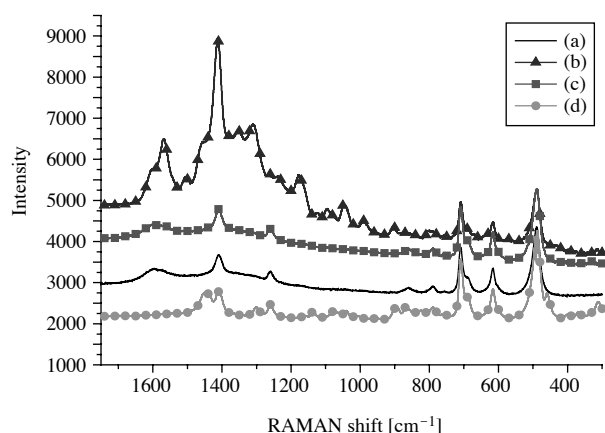


Figure 3. Comparison of RAMAN spectroscopy results: (a) untreated surface, (b) surface functionalized with TMSPMA, (c) surface functionalized in the mixture of perfluorooctane, and TPM (d) surface functionalized in the mixture of heptane, carbon tetrachloride, and TPM.

while the mixture of heptane, carbon tetrachloride, and TPM resulted in a contract angle of 77° (Figure 2d). The last specimen was deformed because the surface area was contracted. Therefore, the functionalization of a PDMS specimen with TMSPMA produced the highest density of hydrophilic components.

RAMAN Spectroscopy

We analyzed the surface properties of four PDMS specimens using a RAMAN spectroscope (NRS-3100, JASCO). The results are as shown in Figure 3. An untreated PDMS surface consisted of Si-O-Si symmetric stretching (490 cm^{-1}), Si-CH₃ rocking (615 cm^{-1}), Si-C symmetric stretching (710 cm^{-1}), CH₃ symmetric bending ($1,260\text{ cm}^{-1}$), and CH₃ asymmetric bending ($1,410\text{ cm}^{-1}$). The Raman shifts for the three functionalized surfaces show a similar trend to that of the untreated surface since the reagents used for the functionalization consist of organic materials. However, the overall intensities of Raman shifts for the functionalized surfaces are stronger than those for the untreated surface, except the case of the surface functionalized in the mixture of heptane, carbon tetrachloride, and TPM. This is caused by inaccurate measurements due to the deformation of the last specimen. The surface functionalized with TMSPMA showed the strongest intensity of a Raman shift for CH₃ ($1,420\text{ cm}^{-1}$) due to -CH₃ groups in the reagent.

Conclusions

We examined three methods to form a self-assembled monolayer on PDMS surfaces which can be uti-

lized for immobilizing a hydrophilic polymer membrane in a PMDS microchannel by covalent bonding. The methods used TMSPMA or TPM reagents for surface functionalization after treating the PDMS surfaces with UV/ozone plasma. Contact angles between a water droplet and functionalized PDMS surfaces decreased due to -OH groups generated on the surfaces. The reagent of TMSPMA resulted in the smallest contact angle of 46°. Raman spectroscopy showed that the intensities of Raman shifts were strongest for the surface functionalized with TMSPMA. Overall, functionalizing a PDMS surface with TMAPMA resulted best among the methods examined in this study. For future work, we are going to immobilize a hydrophilic polymer membrane in a PDMS microchannel using the surface functionalization method with TMAPMA, and to study the stability and durability of the polymer membrane.

Materials and Methods

Chemicals

Sylgard 184A (PDMS prepolymer) and Sylgard 184B (the curing agent) were purchased from Dow Corning (Midland, MI, USA). Reagents of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA), heptane, carbon tetrachloride, hexane, and perfluorooctane for the surface treatments of a PDMS substrate were obtained from Sigma-Aldrich (St. Louis, MO, USA). 3-(trichlorosilyl)propyl methacrylate (TPM) was purchased from Fluka Chemicals (Milwaukee, WI, USA).

PDMS Specimen

Sylgard 184A PDMS prepolymer was mixed thoroughly with the curing agent Sylgard 184B at 10 : 1 (v/v), and was degassed for 10 min at 10 m Torr in a vacuum oven (JSVO-60T, JS Research, Inc.) The polymer was cured for 1-2 hours at 65°C in an oven, and then was cut to a 1 cm × 1 cm square specimen. The PDMS specimen was sonicated in ethanol for 5 min, and was thoroughly rinsed with deionized water.

UV/ozone Treatment of PDMS Specimen

The surfaces of a PDMS specimen were oxidized for 30 min in an UV/ozone cleaner (Model 144AX-220, Jelight Company, Inc.). The cleaner excites contaminant molecules on the PDMS surfaces to react with atomic oxygen continuously generated from molecular oxygen and ozone by 185 nm and 254 nm UV radiations, respectively. The products of the excitation of the contaminant molecules desorb from the surface. This process oxidizes the surfaces to silanol (Si-OH)^{7,9}.

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