



Surface modification of PDMS by atmospheric-pressure plasma-enhanced chemical vapor deposition and analysis of long-lasting surface hydrophilicity

Donghee Lee^a, Sung Yang^{a,b,c,*}

^a Graduate Program of Medical System Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500712, Republic of Korea

^b School of Mechatronics, Gwangju Institute of Science and Technology (GIST), Gwangju 500712, Republic of Korea

^c Department of Nanobio Materials and Electronics, Gwangju Institute of Science and Technology (GIST), Gwangju 500712, Republic of Korea

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ABSTRACT

Atmospheric-pressure plasma-enhanced chemical vapor deposition (AP-PECVD) offers several benefits such as simplicity, high productivity, and versatility. An AP-PECVD-based method is proposed in this study to modify hydrophobic PDMS (polydimethylsiloxane) surfaces towards a long-lasting hydrophilic character. To enhance the sustainability of the hydrophilicity, two kinds of layers were sequentially deposited by AP-PECVD on the surface of a PDMS block (TEOS-O₂/CH₄/PDMS). A hydrocarbon layer was first coated on the bare PDMS surface using CH₄ as the reactant, and then, a hydrophilic SiO_x layer was deposited using tetraethyl orthosilicate and oxygen (TEOS-O₂). The highly cross-linked hydrocarbon layer acted as a physical barrier layer (PBL) between the bare PDMS surface and the hydrophilic layer. To confirm that the PBL suppresses the hydrophobic recovery of the modified PDMS surface with double layer, a single-layer-coated PDMS sample (TEOS-O₂/PDMS) without the PBL was prepared by AP-PECVD using TEOS-O₂. The surface characteristics were determined by static contact angle measurements, surface roughness measurements, and surface chemical composition/chemical bonding determination and compared with those of modified PDMS surface with double layer. The surface morphology of TEOS-O₂/PDMS degraded seriously by the diffusion of PDMS oligomers to the hydrophilic layer, but that of TEOS-O₂/CH₄/PDMS was sustained for a long time. Thus, TEOS-O₂/CH₄/PDMS had the lowest contact angle, almost 0°, and showed long-lasting surface hydrophilicity, with almost no change in the contact angle for 28 days. Thus, this proposed method is confirmed to be well suited for use in applications that require stable hydrophilic surface property in PDMS.

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1. 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 [1,2]. However, because of its innate hydrophobicity, PDMS shows nonspecific binding with biomolecules via physical adsorption [3] and has limited electro-osmotic flow applications [4]. Furthermore, an external mechanical or electrical power source is

required, in general, to support the transport of liquids in a PDMS-based lab-on-a-chip system [5].

Attempts have been made to make the PDMS surface hydrophilic by surface modification, while preserving the bulk-material properties [4–6]. Oxygen-based plasma treatment is a simple and commonly used means of making the PDMS surface hydrophilic, but the hydrophilicity is soon lost because PDMS oligomers migrating from the bulk to the air-surface interface cause hydrophobic recovery within a few hours following the plasma treatment [4,7]. Storing PDMS under water after oxygen-based plasma treatment can reduce the rate of hydrophobic recovery, but this method of storage is not applicable to PDMS-based microfluidic devices [2,8,9]. Thus, increasing the hydrophilicity to the maximum possible extent and preserving it for a long time even when PDMS is stored under dry conditions are critical issues. In addition, the surface modification procedure to be chosen should be simple and cost-effective so that it can be used for large-scale surface modification. Numerous methods such as thermal aging [10], sol-gel coating [11], deliberate protein adsorption [12], layer-by-layer (LBL) deposition [13], silanization [14], and

Abbreviations: AP-PECVD, atmospheric-pressure plasma-enhanced chemical vapor deposition; PDMS, polydimethylsiloxane; TEOS, tetraethyl orthosilicate; PBL, physical barrier layer; LBL, layer-by-layer; PPAA, plasma polymerized acrylic acid; RF, radiofrequency; DOE, design of study; ANOVA, analysis of variance; XPS, X-ray photoelectron spectroscopy; SEM, scanning electron microscopy.

* Corresponding author at: #406 Mechatronics Bldg., GIST, 261 Cheomdan-gwagi-ro, Buk-gu, Gwangju 500712, Republic of Korea. Tel.: +82 62 715 2407; fax: +82 62 715 2384.

E-mail address: syang@gist.ac.kr (S. Yang).

radiation-induced graft polymerization [7,15,16] have been proposed for achieving long-term surface hydrophilicity. Moreover, to inhibit the migration of PDMS oligomers from the bulk to the surface, the physical barrier layer (PBL) concept has been introduced in various surface modification methods such as UV polymerization [17], silanization [18], and chemical vapor deposition (CVD) [19,20]. Plasma polymerization has been used for the surface modification of PDMS by the deposition of a PBL such as a plasma polymerized acrylic acid (PPAA) layer [19]. The wettability and hydrophilicity of the PDMS surface modified using these PBL-based methods are retained for a long time, and the rate of hydrophobic recovery is efficiently decreased [4]. Currently, there is a strong demand for surface modification methods that can induce surface hydrophilicity not only in PDMS but also in synthetic polymers with an inert hydrophobic surface [21,22].

Plasma polymerization that includes plasma-enhanced chemical vapor deposition (PECVD) is widely used for surface modification and thin-film fabrication since it is a gas-phase process in which chemical wastes are not produced, and therefore, washing and drying steps are not necessary. Furthermore, the deposition layer in PECVD can be changed by simply changing the reactant, similar to the case of chemical polymerization, where the nature of the product can be varied by changing the monomer used. Recently, atmospheric-pressure PECVD (AP-PECVD), in which plasma deposition is effected at atmospheric pressure, has gained popularity [23–25]. Since the AP-PECVD apparatus can be operated at atmospheric pressure, no vacuum chamber or pumping system is required; further, there is no limit on the substrate size to be used in AP-PECVD, as opposed to low-pressure plasma-enhanced chemical vapor deposition, in which only small substrates can be employed. In addition, AP-PECVD allows for parallel and in-line processing [26–28].

A stable hydrophobic layer on hydrophilic materials has been previously developed by depositing a hydrocarbon layer on the substrate by AP-PECVD using CH_4 as the reactant [29]. Plasma polymerization yields a highly cross-linked layer by promoting random chemical reactions between various radicals activated by the radiofrequency (RF) plasma in the polymerization step, and the hydrophobicity of the coating layer is retained for more than 4 months. In addition, SiO_x or SiOC layers can be deposited by AP-PECVD using tetraethyl orthosilicate (TEOS) with/without O_2 [24,30,31]. The SiO_x layer is strongly hydrophilic, and hence, it can be used to make the PDMS surface hydrophilic.

In this study, we developed a method for making the hydrophobic PDMS surface hydrophilic by surface modification and ensuring long-lasting hydrophilicity. Two layers were sequentially deposited on a PDMS block via AP-PECVD using CH_4 and TEOS-O_2 reactants. A PBL, the lower layer in the double layer, was first deposited on the bare PDMS surface by using CH_4 as the reactant, and then, a highly hydrophilic layer, the upper layer, was deposited using TEOS-O_2 as the reactant. The combination of two functional layers deposited by AP-PECVD helps in achieving long-lasting hydrophilicity on the PDMS surface, and this double-layer deposition is simple and rapid. On the basis of the idea of surface modification, the optimal processing conditions for double-layer deposition through AP-PECVD were investigated by monitoring the static contact angle, which is related to the rate of hydrophobic recovery. To compare the long-term hydrophilicity after surface modification, four PDMS samples—unmodified PDMS sample, two PDMS samples modified by single-layer deposition (CH_4/PDMS , $\text{TEOS-O}_2/\text{PDMS}$), and the PDMS sample modified by double-layer deposition ($\text{TEOS-O}_2/\text{CH}_4/\text{PDMS}$)—were characterized. The modified PDMS surface was characterized by surface topography analysis, static contact angle measurements, and surface chemical composition/chemical

bonding determination to confirm the effectiveness of the proposed method.

2. Experimental

2.1. Materials

PDMS (prepolymer) and Sylgard 184 (curing agent) were mixed in 10:1 ratio and stirred. Then, 20-g portions of this mixture were poured into a polystyrene Petri dish, 10150 (SPL Life Science Co., Republic of Korea) 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 $2\text{ cm} \times 4\text{ cm}$ pieces and peeled off.

2.2. Surface modification by AP-PECVD

For depositing each layer of the double layer, a commercial AP-PECVD system (IDP-1000; APPlasma Co., Republic of Korea) operating at an RF of 13.56 MHz was utilized. 5% of CH_4 mixed with argon was used as the reactant for the PBL deposition, while a mixture of TEOS (vaporized by 1 slm of argon) and O_2 was used for depositing the hydrophilic SiO_x layer on the PBL. Helium was used as the carrier gas (15 slm for AP-PECVD with CH_4 ; 5–15 slm for AP-PECVD with TEOS-O_2). A 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 samples were mounted on a moving stage positioned below the plasma source; the stage moved at a speed of about 20 mm/s in the orthogonal direction with respect to the plasma source head. The substrate was repeatedly passed back and forth across the plasma head region. This surface modification on each PDMS sample could be completed within 10 min for long-lasting hydrophilicity.

2.3. Design of experiment for optimal processing conditions

The processing conditions that afford long-lasting hydrophilicity of the PDMS surface were determined by design of experiment (DOE). The optimal processing conditions for the double-layer deposition were investigated by monitoring the static contact angle on the seventh day following surface modification, which represented the rate of hydrophobic recovery of the modified surface. A DOE was performed using a standard L_{18} orthogonal array including five factors to identify the optimal processing conditions. A number of controllable factors that may influence the characteristics of plasma deposition were selected. Five of these factors were considered the major ones affecting the wettability; two influenced only the PBL properties, and three were related to the properties of the hydrophilic layer. One of the five factors was selected to investigate the efficiency of the two reactants, CH_4 and vaporized TEOS, in acting as a PBL and inhibiting hydrophobic recovery on the modified hydrophilic PDMS surface. The first factor determined the chemical composition of the PBL. Two factors that affect the thickness of each PBL and hydrophilic layer were chosen by controlling the number of head movements in AP-PECVD. The flow rates of the carrier gas helium and O_2 in the hydrophilic layer deposition were added as factors that would determine the activation ratio of the chemical reaction and the physical bombardment in the atmospheric-pressure plasma field, which in turn influence the physical and chemical properties of the SiO_x layer. When using L_{18} orthogonal array, only 18 cases were required under each set of processing conditions, for accurately evaluating the contribution of each factor to the contact angle. A balanced level of each factor was assigned to each trial, the L_{18} orthogonal array was constructed, and two PDMS samples were considered for each set of

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