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Long-term retention of hydrophilic behavior of plasma treated polydimethylsiloxane (PDMS) surfaces stored under water and Luria-Bertani broth

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ABSTRACT

Polydimethylsiloxane (PDMS) is inherently hydrophobic. Oxygen plasma treatment is a non-toxic, low cost method to render PDMS hydrophilic. Storing PDMS samples, immediately after plasma treatment, under water and Luria-Bertani broth (LB broth), a common growth medium for bacteria, retards hydrophobic recovery considerably. PDMS samples stored in LB broth retain hydrophilic behavior the longest period (contact angle about 10–20° after a week) and the samples stored in water also remained hydrophilic for 7 days (around 20–30°), whereas, the samples stored in air recovered hydrophobicity quickly (above 100° after a week). Scanning electron microscopy (SEM) reveals no clear correlation between wettability and cracks, but changes in surface properties that are not visible through SEM are seen in the drying pattern left on PDMS by the fluid. We show that bacteria (*E. coli* strain MG1655 and any air borne) and the biofilm produced by them have minimal effect on wettability, however sealing the petri dishes during storage further reduce the contact angle.

1. Introduction

Arguably, PDMS is the most popular material that is used for fabricating microfluidic devices [1–4]. PDMS is uniquely suited for biological applications as it is transparent to UV and visible light and the devices are easily replicable. It is permeable to gases such as oxygen and carbon dioxide and has a low toxicity, making it easy to handle. There are a lot of cumulative experiences with PDMS as it is now widely used to fabricate microfluidic devices.

However, one of the major drawbacks of PDMS is that PDMS is inherently hydrophobic (water contact angle ∼109°). The hydrophobic nature poses a problem for driving water through micro-channels without pumps and actuators as well as for binding biological substrates to the surface of PDMS. As a result, several methods of surface modification have been invented which involves corona discharge, UV treatment and chemical coatings [4–7].

Given the economical consequences, there is a great deal of interest in designing a non-toxic, hydrophilic PDMS that can be used for biological applications such as growth of biofilms, cell culture, and retention of biofluids. Amongst the different methods of surface modification, oxygen plasma treatment of modifying the PDMS surface is now widely used as a fast, low-cost, and non-toxic method. Oxygen plasma treatment removes the methyl group and replaces it with polar —OH bonds on the surface of PDMS, creating silanol groups. Oxidation introduces a polar functional group (SiOH) on PDMS surface that then makes a weak bond with water molecules and thus PDMS becomes hydrophilic [8,9]. Another result of plasma treatment is that irregular nano-cracks appear on the surface of PDMS [10]. It is speculated that the cracks increase the roughness of the surface, contributing to the hydrophilic modification [11].

However, PDMS eventually regains its hydrophobic nature, and this has been attributed to diffusion of low molecular weight (LMW) chains from the bulk to surface. Its elastomeric properties allow PDMS to recover hydrophobicity. Removal of the LMW chains results in a slower hydrophobic recovery [12]. PDMS samples stored in air after oxygen plasma treatment can regain hydrophobicity quickly. To retard the rapid hydrophobic recovery, chemicals are grafted onto the modified surfaces of PDMS [13]. However, addition of a chemical coating of the modified surface layer on PDMS can be problematic in many uses and may cause chemical incompatibility with the fluids and especially biological materials, reducing the attractiveness of PDMS. Since growth medium Luria-Bertani (LB) broth is a complex material, which contains proteins and salt, it is important to determine its influence on the hydrophilic nature of PDMS. To our knowledge, this is the first study done on the effects of storage under a growth medium.

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While plasma treatment makes the surface hydrophilic, the question of its stability is of supreme importance. Many biological studies require the use of a micro fluidic device for several days. A different method of delaying hydrophobic recovery is to select different storage conditions. Studies show that storing PDMS samples in water after plasma treatment has an effect on hydrophobic recovery [14,15].

However, there is a lack of study done comparing the effects of storage conditions on hydrophobic recovery. In this work, we demonstrate that hydrophilic nature of plasma treated PDMS is durable if the sample is not taken out of water as opposed to exposed in air for measurements. In addition, we demonstrate that there is no clear correlation between hydrophobic recovery and the cracks in contrast to other studies [11].

The present work, in some ways, complements and extends that of Lawton et al. [14] but our emphasis is different. Lawton et al. [14] tested the contact angles of water on oxidized 30 nm PDMS films that were immediately stored, after plasma oxidation, in air, in water, and in hexadecane after plasma treatment. Lawton et al. [14] speculate that the thickness of the PDMS has a major role in hydrophobic recovery time.

We use rather thick PDMS samples more representative of microfluidic devices. For silicone rubber a study similar to ours was done by Everaert et al. with similar motivation for biomedical/materials science applications [16]. Here, we measured contact angles of water on oxidized PDMS samples that were stored in air, water, and LB broth immediately after plasma treatment.

We were initially motivated by the conditions under which biofilms grow on PDMS. Our preliminary work has shown qualitatively that biofilm growth is retarded on untreated PDMS while it is normal on the plasma treated PDMS. A quantitative study of this will be reported later. It has been shown by Chandra and Patel that surface modification plays an important role in bacterial adhesion and biofilm growth on surface [17]. Therefore, we expect that PDMS wettability studies will be valuable for understanding bacterial growth, adhesion and biofilm formation. However by doing a set of careful experiments, we do not find much influence of bacteria per se. We have used MG1655 *E. coli* strain (obtained from the Yale University *E. coli* genetic stock center) that is known to be prolific biofilm producers [18]. However, keeping the petri dishes (that house the submerged samples) sealed by parafilm helps to reduce the contact angle and increase wettability.

After completion of this work, we noted that a paper by Ma et al. [19] is scheduled to be published in November 2011 on wettability control and patterning of PDMS using UV-ozone and water immersion. UV ozone treatment is similar to the plasma treatment used here except that the former is a much slower process. Ma et al. also notice substantial effect of suppression of hydrophobic recovery upon storage under water. They also find some interesting effect of curing time for UV ozone treatment. The impact of curing time on wettability for plasma treatment will be considered elsewhere.

2. Materials and methods

2.1. PDMS preparation

Sylgard® 184 Silicone Elastomer Kit from Dow Corning was used for preparing PDMS. The base and curing agent were mixed in a 10:1 weight ratio and centrifuged for 5 min in order to remove air bubbles from the mixture. Approximately 7 mL of the mixture was poured onto each petri dish for uniform thickness. The thickness of all PDMS pieces in this study is controlled at 1.14 ± 0.36 mm. Then the PDMS were heat-cured in 80 °C for an hour.

We have studied the hydrophobic recovery using three different Groups (protocols)—Group 1 is to emphasize the effect of storage medium, the second Group is to emphasize the effect of air exposure during the contact angle measurement and the third Group is to study the effect of bacteria—both from unspecified aerial bacteria, if any, and from a well known strain *E. coli* MG 1655. In Group 1, even if the samples are retuned to the fluid, the hydrophobic recovery was quick. We hypothesized that once the sample was taken out of fluid within 10 min the hydrophobic recovery was inevitable. We designed Group 2 to test this hypothesis and we found indeed that storing under water and LB broth for a long time indeed preserves hydrophilic behavior. In Group 3 we show the effect of bacterial on wettability of PDMS is minimal.

2.1.1. Group 1: effect of storage medium

The effects of the storage medium in hydrophobic recovery retardation were studied by placing samples into petri dishes with air, de-ionized water, or LB broth after plasma treatment. Each of the three petri dishes had 6 samples of PDMS that were labeled M5, M10, M15, H5, H10, and H15. The letter M or H denotes whether the PDMS samples were plasma treated in medium power or in high power, respectively. The number following the letter M or H denotes treatment time in minutes.

2.1.2. Group 2: effect of air exposure during storage

The difference between air-exposed samples and non air-exposed samples in hydrophobic recovery was demonstrated in this protocol. The petri dishes were labeled WM5, WM10, WM15, WH5, WH10, WH15, BM5, BM10, BM15, BH5, BH10, and BH15. The first letter W or B denotes whether the PDMS samples were stored in water or in LB broth, respectively. The second letter M or H denotes whether the PDMS samples were plasma treated in medium power or in high power, respectively. The number following the letter M or H denotes treatment time in minutes. The PDMS in each petri dish was cut into 16 pieces that were used for different time measurements (time lapsed after plasma treatment). In order to compare the effects of air exposed samples and non-exposed samples in hydrophobic recovery, each petri dish contained a piece of a sample which was exposed to air during the contact angle measurement (denoted as AE) and was placed back into its petri dish after each measurement. Other 14 samples were measured after 10 m, 20 m, 30 m, 1 h, 2 h, 4 h, 6 h, 24 h, 48 h, 72 h, 96 h, 120 h, 144 h and 168 h of treatment. These samples were disposed of after air exposure during the contact angle measurement. One sample (denoted T) was kept submerged for 24 h before any measurements were made on it. Like the sample AE it was returned after the contact angles were measured for each time increment (after 24 h of initial submersion under water or LB broth) to see a change in contact angles and then returned to the petri dish. For example, a petri dish that had 16 samples submerged in water after plasma treating them in high power for 15 min was categorized as WH15. The 16 samples were labeled as AEWH15, WH15 (10 m), WH15 (20 m), WH15 (30 m), WH15 (1 h), WH15 (2 h), WH15 (4 h), WH15 (6 h), WH15 (24 h), WH15 (48 h), WH15 (72 h), WH15 (96 h), WH15 (120 h), WH15 (144 h), WH15 (168 h), and TWH15.

2.1.3. Group 3: effect of bacteria or biofilm on the hydrophilicity of PDMS

For the Groups 1 and 2, we stored the samples in LB broth in one petri dish, i.e. one petri dish for all samples in Group 1 and another petri dish for all the samples Group 2, in order to keep the samples under the same condition prior to the contact angle measurements on the samples. On the other hand, the fluids in which the samples are immersed are exposed to air every time the petri dish is opened (and then closed) to take a sample out. In addition the sample T and AE are returned to the LB broth after contact angle measurements.

In order to test if any unspecified aerial bacteria contamination indeed played any role in reducing the contact angle, we run