A LONG-TERM, STABLE HYDROPHILIC POLY(DIMETHYLSILOXANE) COATING FOR CAPILLARY-BASED PUMPING

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ABSTRACT

Hydrophilic surfaces are highly desirable for transporting liquids within microchannels. However, creating stable hydrophilic surfaces on poly(dimethylsiloxane) (PDMS) is a challenging feat. We present a straightforward method for generating stable hydrophilic coatings in which poly(ethylene glycol) (PEG) is bonded to PDMS through a 3-step fabrication process. The resulting surfaces are rendered hydrophilic having a contact angle of 17° ± 2°. Additionally, this coating exhibits long-term stability maintaining a contact angle < 22° for at least 47 days. Various PEG-coated PDMS microchannels were fabricated for flow characterization studies and for demonstrating the effectiveness of this technique for on-chip fluidic processing.

INTRODUCTION

The eventual realization of portable, inexpensive and user-controllable lab-on-a-chip (LOC) systems will require autonomous liquid delivery and transportation without externally powered pumps or valves. PDMS is one of the most popular materials for fabricating microfluidic devices, in part due to its low cost, widespread availability and ease of fabrication. However, untreated PDMS is very hydrophobic (water contact angle ~109°), requiring external pumps or on-chip actuators to drive liquids through microchannels. These components require external power sources which are bulky and expensive, thereby presenting a major roadblock for the miniaturization of hand-held LOC systems. By rendering the surface of PDMS hydrophilic with long-term stability, the need for pumps can be eliminated, thus enabling for the development of portable and reliable LOC systems. One widely used approach for creating hydrophilic PDMS surfaces involves exposure to an air or O_2 plasma [1-3]. However, the effects of these treatments are temporary and the surface reverts back to a hydrophobic state within a few hours [4]. Additionally, a variety of hydrophilic coatings on PDMS have been demonstrated [5-8]; however, these treatments involve long and complicated fabrication processes, require the use of inaccessible or expensive machinery, dramatically change the bulk PDMS properties and/or lack long-term surface stability.

In this work, we have developed a method for creating stable, hydrophilic coatings in which PEG is bonded to PDMS using a simple 3-step fabrication process (Fig. 1). This coating process can be completed in less than 30 min and results in highly hydrophilic PEG-PDMS surfaces which exhibit a water contact angle of 17° ± 2°. In addition to being hydrophilic, PEG is non-toxic and offers exceptional biocompatibility, making it an ideal material for biological applications. Surface characterization of PEG-coated PDMS was performed using atomic force microscopy (AFM) (to observe surface topography and coating uniformity) and contact angle measurements (to determine hydrophilicity and study long-term stability). PEG-PDMS microchannels were utilized to demonstrate capillary-driven flows and common fluidic processes, which could be performed without the use of on-chip or externally powered actuators.

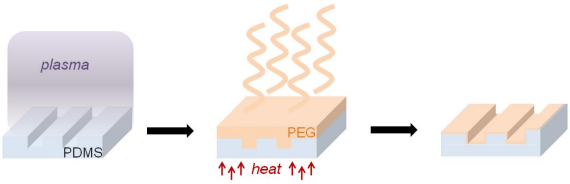

Figure 1. Schematic illustration of the PEG-coating process for generating hydrophilic surfaces on PDMS microchannels. The 3-step fabrication process can be completed in less than 30 min.

MATERIALS

Silicon wafers were purchased from Techgophers (Los Angeles, CA) and microscope glass slides were purchased from Fischer Scientific (Tustin, CA). PDMS prepolymer and curing agents (Sylgard 184) were obtained from Dow Corning (Midland, MI) and PEG (MW 200) was obtained from Sigma-Aldrich (St. Louis, MO). Food coloring used for flow visualization was obtained by Tone Brothers (Ankeny, IA). Acetone, isopropanol and methanol (Gallade Chemical), AZ 4620 photoresist (Shipley Corporation), piranha solution and deionized water were provided by the Nanoelectronics Research Facility at the University of California, Los Angeles.

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METHODS

PDMS/Device Fabrication

PDMS molds were fabricated on silicon wafers cleaned in a Piranha bath to ensure proper adhesion of photoresist. Photolithography was performed to pattern AZ 4620 photoresist as an etch mask for subsequent deep reactive ion etching (Unaxis Versaline). PDMS prepolymer and curing agents were mixed and degassed, poured onto the silicon molds, cured for 2 hr at 80°C and cut into individual chips. Inlet and outlet holes were punched using stainless steel needles and cylindrical tubes. Microfluidic devices were formed by bonding surface-modified PDMS chips to glass slides cleaned in isopropanol and deionized water. PDMS specimens for surface characterization were cured in polystyrene Petri dishes and cut into 1 cm x 1 cm pieces.

Surface Modification

PDMS chips were cleaned in isopropanol and deionized water, dried with compressed air and placed in a Harrick air plasma cleaner/sterilizer (PDC-002) for 90 seconds with the radio frequency set to high. PEG was immediately applied to the oxidized PDMS surfaces and the chips were placed onto a hot plate set at 150°C for 25 min. Chips were cooled, washed with isopropanol and water to remove residual PEG and dried.

AFM Measurements

Surface topography of PDMS specimens were captured in air using a Digital Instruments MultiMode Scanning Probe Microscope (SPM) with a Nanoscope 3A controller (Santa Barbara, CA) operating in tapping mode. Specimens were mounted onto steel discs, which were magnetically attached to the stage. Silicon probes (Veeco Probes, Camarillo, CA) were used with a typical tapping frequency of 240–280 kHz and a nominal scanning rate of 0.8–1.0 Hz. Three scans were performed for each specimen and images were processed and analyzed using Digital Instruments Nanoscope R IIIa software.

Contact Angle Measurements

Static water contact angle measurements were obtained using a First Ten Ångstroms FTÅ4000 contact angle analysis system (Portsmouth, VA). Deionized water droplets of 5 µL were manually deposited onto the specimens using a 10 µL Eppendorf pipette. Six measurements were made for each specimen and analyzed using the system's FTA Video software. All the specimens were stored in polystyrene dishes at room temperature and humidity and fresh specimens were used for each measurement.

Flow Characterization and Device Operation

PEG-PDMS microchannels were fabricated to characterize fluid flows and demonstrate device applicability. Liquids were manually loaded into the inlets of the microchannels using a pipette and were solely driven by capillary force. For enhanced visualization, microchannels were filled with colored dyes, which were diluted at a ratio of 5:1 (DI water:dye). Still and video images were captured using a Canon Digital IXUS 75 camera (Lumos Technology, Taipei, Taiwan).

RESULS AND DISSCUSSION

Surface Characterization

Three-dimensional tapping mode AFM scans were performed on untreated and PEG-coated PDMS specimens to detect changes in surface topography as a result of the surface treatment. Untreated PDMS (Fig. 2A) exhibits flat and uniform surfaces having a root mean square roughness (rms) 0.61 nm. In contrast, PEG-coated PDMS (Figs. 2B) exhibits large hill and valley-like features, which result from the formation of PEG layers bonded to the surface. Additionally, PEG-PDMS surfaces have a higher rms value of 5.1 nm. Multiple scans at various locations on the PEG-coated specimens revealed similar features demonstrating uniform surface coverage. To account for the robustness of the PEG coating, we hypothesize that the heat treatment process increases the rate at which molecular bonding occurs and/or enhances the adhesion strength of PEG to the surface. Additionally, the PEG coating provides a barrier against hydrophobic groups from migrating up to the surface, which improves the longevity of the coating and enables for highly-wettable surfaces for capillary-driven flows.

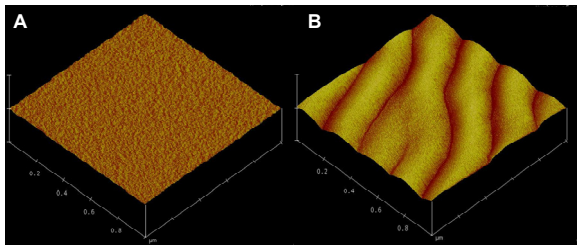

Figure 2. AFM tapping mode images of (A) untreated PDMS and (B) PEG-coated PDMS. Surface-treated PDMS exhibits distinctive hill-like features, representing attached PEG chains, whereas untreated PDMS exhibits a smoother profile. The scan size is 1 µm x 1 µm.

Contact angle measurements were performed to further characterize the PEG coatings and to monitor the stability of its wetting characteristics. For untreated PDMS, the contact angle is 110° ±

2°, which is consistent with published values [9]. Plasma-treated PDMS (3 min, high radio frequency) exhibits a contact angle of 15° ± 3° whereas PEG-coated PDMS exhibits a contact angle of 17° ± 2°. To assess the stability of the PEG-coating, contact angle measurements were taken over the course of 47 days (Figure 3). Although plasma-treated PDMS exhibits the lowest contact angle of all the specimens, it also experiences the quickest hydrophobic recovery (< 1 hr). In contrast, PEG-coated PDMS exhibits contact angles < 18° for the first 14 days and gradually stabilized at ~ 22°. This slight inclination in contact angle can be attributed to surface contamination due to airborne particles during storage. These results are consistent with AFM analyses, which suggest that the thickness and coverage uniformity of the PEG coating contribute to its long-term stability. Additionally, the long-term contact angle measurements provide insight into the durability of these coatings, which is of particular interest when considering the shelf-life of microfluidic devices incorporating such surface treatments.

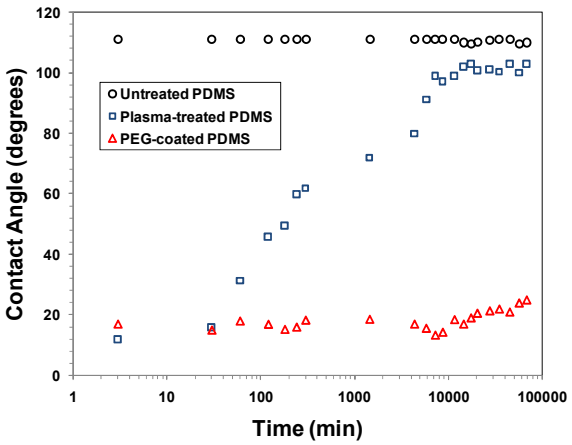

Figure 3. Long-term stability of PEG-coated PDMS surfaces. A conventional treatment of PDMS by plasma exposure yields relatively short-term surface stability (i.e. ~1 hr), as opposed to our proposed surface treatment in which a surface stability of ~50 days can be achieved. Untreated PDMS exhibits a contact angle of ~109°.

Flow Characterization

Straight microchannels (115 µm in height and 23 mm in length) of varying widths were fabricated and utilized for flow characterization studies. Due to the hydrophilic nature of the PEG-PDMS surfaces, liquids readily filled the microchannels by capillary force. Microchannels having widths between 50 µm and 1 mm were analyzed to observe the influence of channel size on the flow rate. As shown in Figure 4, the flow rate is proportional to the channel diameter, which is consistent with the predicted behavior of liquids filling rectangular capillaries [10]. These results reveal that the proposed hydrophilic coating remains effective in driving liquids, even as the channel diameter is enlarged. Additionally, capillary-driven flows have the advantage of producing predetermined flow rates which can be controlled by the channel geometry. Based on our results, we propose that PDMS microfluidic networks can be designed for applications requiring precise flow rates or timed fluidic processes and reactions by modifying the channel dimensions.

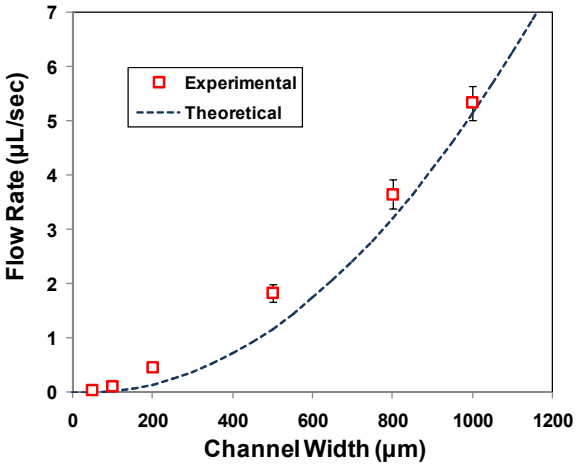

Figure 4. Volume flow rate as a function of channel width in PEG-coated PDMS microchannels. Microchannels of varying widths with constant height and length, 115 µm and 23 mm respectively, were analyzed.

On-chip Fluidic Processing

The proposed technique provides a simplified means of creating hydrophilic PDMS surfaces which allows for fluidic processes to be performed within microchannels solely by capillary force. In particular, sample loading is greatly simplified where liquids can be accurately controlled and dispensed by a pipette. Such a technique is highly advantageous for microfluidic devices with multiple inlets since separate pumps are usually required for each inlet, which greatly increases the complexity and bulkiness of the system. Additionally, precise coordination of flow rates with multiple pumps is extremely challenging. Using our approach, flow rates can be synchronized by designing channels with similar dimensions and simultaneously dispensing liquids (Fig. 5). For the two and three-inlet devices presented in this report, the flow rates were observed to be identical, thereby enabling for simultaneous loading of multiple fluids for enhanced automation.

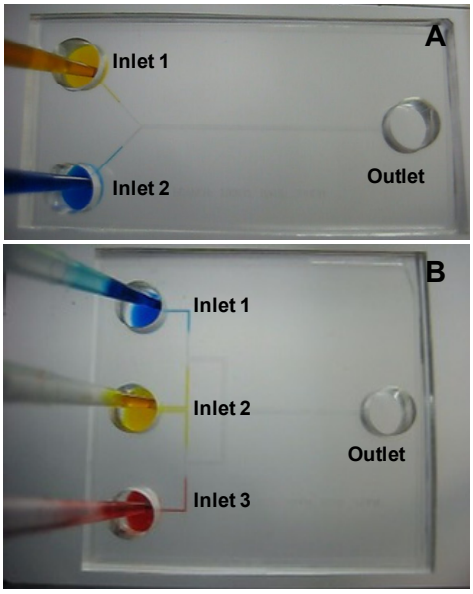

Figure 5. Simultaneous loading of multiple fluids for enhanced automation; (A) dual-loading and (B) tri-loading. Fluids are manually dispensed into the inlets using a multi-channel pipette. Colored dyes are used for enhanced visualization.

In addition to characterizing flows in straight channels, microfluidic devices were fabricated to demonstrate the feasibility of utilizing the proposed PEG coating to drive liquids for basic fluidic processes. Passive mixing and concentration gradient generation were successfully demonstrated using colored dye (Fig. 6). In both of these devices, liquids were simultaneously dispensed into inlets 1 and 2 via pipetting. Similar to the straight microchannels, liquid quickly filled these devices allowing for rapid on-chip fluidic processing. Careful design of the channel geometries allows for precise control over the process parameters (i.e., gradient profile, mixing efficiency, etc.). Based on these results, it would be possible to design functional LOC systems which are fully automated and solely driven by capillary flows.

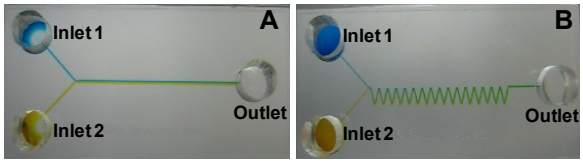

Figure 6. PEG-coated PDMS devices demonstrating (A) concentration gradient generation and (B) passive mixing. Sample loading was achieved by manually pipetting liquids into the inlets. Microchannels are filled with colored dyes for enhanced visualization.

CONCLUSIONS

A simple and rapid fabrication process for generating PEG coatings on PDMS surfaces with long-term stability has been demonstrated. The presented approach consists of three steps which can be completed in less than 30 min. Characterization of the coatings revealed high stability where PEG-PDMS surfaces exhibited water contact angles < 23° for at least 47 days. Straight microchannels and microfluidic devices were fabricated and utilized to characterize the fluid flows and showcase basic fluidic processes that can be performed using the presented surface modification technique. In summary, this process greatly simplifies the fabrication of passive pumping microfluidic devices and allows for the development of lab-on-a-chip systems which are portable, reliable and simple to operate.

ACKNOWLEGEMENTS

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REFERENCES

[1] D.C. Duffy, J. C. McDonald, O. J. A. Schueller and G. M. Whitesides, *Anal. Chem.*, 70, pp. 4974-4984, 1998

[2] E. Delamarche, A. Bernard, H. Schmid, B. Michel and H. Biebuyck, *Science*, 276, pp. 779-781, 1997

[3] R. A. Lawton, C. R. Price, A. F. Runge, W. J. Doherty III and S. Saavedra, *Colloids Surf., A*, 253, pp. 213-215, 2005

[4] J. L. Fritz and M .J. Owen, *J. of Adhes.*, 54, pp. 33-45, 1995

[5] H. Makamba, J. H. Kim, K. Lim, N. Park and J. H. Hahn, *Electrophoresis*, 24, pp. 3607-3619, 2003

[6] J. Liu and M. L. Lee, *Electrophoresis*, 27, pp. 3533-3546, 2006

[7] A. Muck, and A. Svatoš, *Talanta*, 74, pp. 333-341, 2007

[8] I. Wong and C. M. Ho, *Microfluid. Nanofluid.*, 7, pp. 291-306, 2009

[9] J. A. Vickers, M. M. Caulum and C. S. Henry, *Anal. Chem.*, 78, pp. 7446-745, 2006

[10] M. Zimmermann, H. Schmid, P. Hunziker and E. Delamarche, *Lab Chip*, 7, pp. 119-125, 2007