Applied Surface Science 257 (2010) 451–457

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Long term hydrophilic coating on poly(dimethylsiloxane) substrates for microfluidic applications

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ARTICLE INFO

Article history:
Received 23 February 2010
Received in revised form 1 June 2010
Accepted 5 July 2010
Available online 13 July 2010

Keywords:
Poly(dimethylsiloxane) (PDMS)
Plasma oxidation
Polyethylenimine (PEI)
XPS
Surface modification
Contact angle

ABSTRACT

Poly(dimethylsiloxane) (PDMS) has been used extensively for microfluidic components and as substrates for biological applications. Since the native nature of PDMS is hydrophobic it requires a functionalization step for use in conjunction with aqueous media. Commonly, oxygen plasma treatment is used for the formation of hydrophilic groups on the surface. However, the hydrophilic nature of these surfaces is short lived and the surfaces quickly revert back to their original hydrophobic state. In this work, branched-polyethylenimine (b-PEI) was used for long term modification of plasma treated PDMS surface. Contact angle, X-ray photoelectron spectroscopy (XPS) and Atomic force microscopy (AFM) were used for characterization of the modified surfaces and their stability with time was studied. The results obtained demonstrate that comparatively higher stability, hydrophilic, positively charged surfaces can be obtained after b-PEI treatment. These b-PEI treated PDMS surfaces can be used as fluidic channels for the separation of molecules as well as a substrate for the adherence of bio-molecules or biological cells.

1. Introduction

The advent of miniaturization, has led to the large-scale applications of lab-on-a-chip structures in chemical, biological and medical applications, mainly for analytical purposes. There are many-fold advantages of such structures, which include, but are not limited to, reduced analysis time, lesser consumption of reagents, low sample volume requirement, easy integration [1–3], etc. The development of these devices with traditional silicon based MEMS processes is limited by considerations of cost of substrate and its processing which requires, access to clean rooms, and the difficulty of integration of different modules. The rise in number of applications of MEMS devices, specifically for BioMEMS applications, has led to the use of alternative materials like polymers, which are easy to machine, flexible, low in cost and biocompatible. Some of the commonly used polymers are polymethyl-methacrylate (PMMA), poly(dimethylsiloxane) (PDMS), polycarbonate (PC) and polyvinylchloride (PVC) [4–11].

Among various polymers, PDMS has gained wide popularity due to ease in fabrication by rapid prototyping, reproducible features down to sub-micron levels, biocompatibility, chemical inertness, optical transparency down to 280 nm range, gas permeability, electrical resistivity and its property to seal to self and to other substrates. PDMS is comparatively more suitable for developing complex networks of channels and incorporating components like valves and pumps in the same device [12–17]. However, in spite of the many inherent advantages of PDMS, its surface is very hydrophobic, with a contact angle of 110°, making filling of channels difficult with aqueous solutions, and adsorbing bio-molecules and hydrophobic molecules irreversibly. This also leads to sample loss, diminished resolution and less efficient separation in electrophoretic devices [14,18,19]. Unmodified PDMS surfaces generate poorly defined and non-uniform electroosmotic flow, due to the absence of ionizable surface moieties. Thus, a protein resistant, hydrophilic coating or surface group modification, which can impart cationic, anionic or neutral charge to surface, is essential for the application of PDMS in microfluidic applications.

A number of methods have been adopted to make PDMS surfaces hydrophilic. One of the commonly used processes is by exposing PDMS surface to oxygen plasma, ultra-violet light and corona discharge. This method oxidizes surface methyl groups to hydroxyl groups. The inherent limitation with this process is that the surface reverts back to its natural hydrophobic state within few hours, when in contact with air, due to the migration of low molecular weight polymer chains from the bulk to the surface [20–23]. To meet the specific requirements of microfluidic applications, PDMS

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doi:10.1016/j.apsusc.2010.07.010

surfaces can be modified by chemical modification or physical masking using adsorption or dynamic coating. Dynamic coating can degrade during electrophoresis and also pose limitations when detectors are miniaturized and coupled with the fluidic channels. Covalently modified surfaces have been achieved by silanization, radiation induced grafting of polymers, sol-gel method, cerium (IV) catalysis, chemical vapor deposition, phospholipid bilayer modification and layer by layer assembly of polyelectrolyte layers (PEMs) [14,24–36]. Most of these methods form silica like layer or deformations and possess less stable hydrophilic surfaces. The silanol groups bound to such surfaces are prone to reorganization due to migration of polymer chains from the bulk.

In the present work, amine functional groups containing polymer, branched-polyethylenimine of high molecular weight, has been used after the PDMS surfaces were plasma oxidized. The PEI polymeric layer differs from other polymers by the fact that it bears a positive charge on the surface, due to the presence of amine groups. It has a wide range of pH stability and can be used for the efficient separation of basic proteins and reduce adsorption [37]. This study was undertaken to obtain long term hydrophilic and protein resistant surfaces, which is the essential pre-requisite characteristic for any fluidic and biological molecules related experiments. The modified surfaces are studied using surface sensitive techniques of characterization like, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact angle. The stability of the modified films in terms of their hydrophilic character was studied with time by contact angle measurements.

2. Experimental methods

2.1. Materials

Sylgard-184, a silicon elastomeric PDMS kit, containing two parts (base and a curing agent) was purchased from Dow Corning, Polyethylenimine (PEI) with a mean molecular weight of 20,000 and octadecyltrichlorosilane (OTS) was purchased from Sigma–Aldrich Chemicals. PEI used in this work is branched and water free. It contains primary, secondary and tertiary amines in a ratio of 1:2:1, respectively. Millipore de-ionized (DI) water, with a resistivity of 18.2 MΩ-cm is used for rinsing and cleaning. Sulfuric acid, hydrogen peroxide, methanol and iso-propyl alcohol (IPA) (CMOS grade) were purchased from J.T. Baker.

2.2. Fabrication of substrates

Sylgard-184 PDMS base polymer was mixed with its curing agent in a ratio of 10:1 (w/w). This mixture was mixed thoroughly in a teflon beaker with a glass rod and was degassed in vacuum to remove entrapped air bubbles. Piranha cleaned silicon wafers were silanized in a vacuum dessicator with vapors of octadecyltrichlorosilane for 2 h. The chlorosilanization helped in making the surface of silicon hydrophobic and thereby the peeling of PDMS films easy. 1 mm thick sheet of PDMS was formed by pouring the degassed pre-polymer onto a silanized silicon wafer. It was then heated at 75 °C for 3 h for curing. Following this, the flat PDMS sheet was peeled and cut into 1 cm × 2.5 cm samples. The pieces were ultrasonically cleaned with iso-propyl alcohol (IPA) and DI water for 5 min successively.

2.3. Modification of PDMS substrates

The resulting PDMS substrates were subjected to oxygen plasma in a home made barrel type, capacitive coupled RF discharge at 13.5 MHz, and chamber pressure of 1×10^{-5} mbar. In this study, a constant flow rate of oxygen (99.99% pure) was maintained such that the working vacuum of 200 μbar is achieved. 50W RF power was applied using a manually controlled power matching network for 70 s. The time and energy was chosen on the basis of optimization exercise done previously. To prolong the effect of surface modification, the oxidation step was followed by a chemical derivatization step with b-PEI. For this, freshly oxidized PDMS samples were immersed immediately in 10% (w/v) of b-PEI in methanol and heated at 70 °C for 3 h in argon ambient. The samples were washed with DI water and left immersed in DI water for 3 h to remove any loosely adsorbed b-PEI. The drying of the samples was done in argon to remove any traces of water before characterization.

2.4. Contact angle measurements

Contact angle was measured at each step of surface modification procedure with water of resistivity 18.2 MΩ-cm as probe liquid at room temperature, using a static water droplet. Digidrop (model-DS) system was used for the measurements. A 1.5 μl drop of de-ionized water was dropped from a calibrated micro-syringe. Three measurements were taken on each of three samples yielding a total of nine measurements, which were then averaged. The contact angles were also measured as a function of time for five days, with a time interval of 3 h in the beginning, 12 h during intermediate stages and then 24 h at the end.

2.5. AFM

Surface topography was studied using atomic force microscopy (AFM) (Nanoscope III, Digital Instruments). Images were acquired in air using tapping mode, as the polymers can contaminate the tip of the cantilever in contact mode. The phosphorous doped silicon cantilevers (Veeco Instruments) used had a spring constant of 20–80 N/m and resonating frequency of 322 kHz. Images were recorded at a scan rate of 2–4 Hz using a 100 μm × 100 μm scanner.

2.6. X-ray photoelectron spectroscopy (XPS) measurements

To examine possible changes in surface composition after each modification step, the PDMS surface was analyzed with an XPS instrument (Perkin-Elmer Model 1257). The system was operated at a chamber base pressure of 6×10^{-10} mbar. The system was equipped with dual anode and photoelectrons were detected with a hemispherical analyzer positioned at 75° with respect to the normal of the sample surface. Monochromatic Mg Kα (1253.6 eV) radiation was used for the present analysis. The binding energy was calibrated with respect to contaminant free Ag 3d line using Mg Kα as the incident photon. The wide survey scans were acquired using a 100 eV pass energy at an energy step of 1.0 eV, while C1s and N1s individual high resolution, core level spectra were acquired at 0.03 eV energy step with a pass energy of 60 eV. The peaks were fitted with Gaussian function so as to obtain the concentration of various chemical states of carbon and nitrogen.

3. Results and discussion

PDMS treated with b-PEI directly, has physically adsorbed b-PEI which forms a relatively less stable coating onto the surfaces. To increase the stability of b-PEI on the PDMS surfaces, the surfaces were first modified using oxygen plasma and thereafter b-PEI was attached onto the plasma treated surfaces using heat as an activator. The plasma oxidation step enhances the bonding of b-PEI due to the formation of silanol bonds on PDMS surface. The probable reaction mechanism for plasma oxidation of PDMS and the attachment of b-PEI to the oxidized surfaces is shown in Fig. 1.