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Perfluorinated poly(dimethylsiloxane) via the covalent attachment of perfluoroalkylsilanes on the oxidized surface: Effects on zeta-potential values

Peiling Sun [1], J. Hugh Horton *

Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

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ABSTRACT

Poly(dimethylsiloxane) (PDMS) is a widely-used polymer in microfluidic devices due to its range of physical and chemical properties suitable for molding micron-sized features. However, its hydrophobicity also leads to some limitations: it poorly supports electro-osmotic flow, and can be incompatible with biomolecules and with many organic solvents. Surface modification is commonly used to vary PDMS surface properties to make it more suitable for specific microfluidic applications. Here, we report on the surface modification of PDMS using perfluoroalkane–triethoxysilanes, via the covalent attachment of triethoxysilane groups on plasma-oxidized PDMS. A device constructed from such fluorinated materials could be used for separating fluorous-tagged proteins or peptides. Modified PDMS were characterized using a range of surface analytical methods. In particular, zeta- (ζ-) potential values at the interfaces of both modified and unmodified PDMS and under varying pH conditions were measured, as ζ-potential is an essential parameter to support electroosmotic flow (EOF), a common pumping method in microfluidic devices. The results showed the length of fluorinated alkane chain has significant effect on the density of surface modifying species and topography following modification. In addition, the perfluorinated modification increases the magnitude of the ζ-potential at the PDMS interface when compared to that of native PDMS, increasing the electro-osmotic flow rate, over a wide pH range. The modified surface is resistant to the diffusion of PDMS oligomers that affects other PDMS surface modification processes.

1. Introduction

Glass and silicon, originally used to construct microfluidic devices, have the drawback of being relatively expensive to fabricate due to the photolithographic and etching processes required. Investigators have explored a range of polymeric materials as alternatives for fabrication of microfluidic devices, including polymethylacrylate, polyesters, polystyrenes and silicones [1]. Of these, polydimethylsiloxane (PDMS) [2] shows some of the greatest promise. It is easily molded at the micrometre and sub-micrometre level using soft lithography techniques. It is nontoxic, optically transparent, electrically resistive, flexible, gas-permeable and inexpensive [3–8]. Importantly, PDMS is unique in that it can be sealed to itself and other materials without an adhesive immediately following plasma-oxidation [9].

However, the use of PDMS in microfluidic devices has some limitations: its hydrophobic surface may adsorb other such species, it swells in many organic solvents, it absorbs small molecules into its bulk, and under some pH conditions it exhibits a low zeta- (ζ-) potential and consequently may not sufficiently support electro-osmotic flow (EOF), an indispensable requirement for electrokinetic pumping in microfluidic devices. Furthermore, water may diffuse through the bulk PDMS, drying out the interior channels [2–6]. Hence, further surface modification of PDMS is necessary, in particular if a charged surface, and consequently a high magnitude ζ- potential, is to be realised. UV–ozone and plasma oxidation are two methods commonly used to introduce surface silanol groups onto the PDMS surface, increasing both its hydrophilicity and surface charge, through the introduction of a thin silicon oxide overlayer [10]. This brittle overlayer frequently cracks, allowing lower molecular weight PDMS oligomers to diffuse, often within only several hours, to the surface region, and the PDMS once again becomes hydrophobic [11]. This process allows the PDMS surface to regain its intrinsic, relatively low surface free energy of 22–25 mJ m^{-2} [12]. Thus, further modification is usually necessary after oxidation if higher surface free energies are to be maintained.

* Corresponding author. Tel.: +1 613 533 2379; fax: +1 613 533 6669.
E-mail address: jhh@queensu.ca (J.H. Horton).
[1] Current address: Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

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While a wide range of procedures have been reported [13], an important means of modification relies on the hydrolysis reaction of trichloro- or trialkoxysilane species with SiOH surface sites to form a covalently-bound polysiloxane layer. Using this process, PDMS surfaces have been fabricated with a range of functional groups, including amines, mercaptans, carboxylic and sulfonic acid [14,15]. Here, we focus on the formation and characterization of PDMS surfaces modified with perfluorinated alkanes [16]. A device modified with a perfluorinated surface layer is of interest, as it may form the basis of separating fluorous-tagged proteins or peptides [17]. We have previously reported on the use of fluorinated PDMS microfluidic devices which proved successful in selectively adsorbing a fluorinated cortactin derivative [18]. One surprising observation was that perfluorinated PMDS exhibited a zeta potential greater than that of unmodified PDMS, and hence could maintain electro-osmotic flow under a range of pH conditions. Using the current-time monitoring method [19], here we report on the ζ-potential of perfluorinated PDMS prepared under a range of conditions, correlating these measurements to observations of the PDMS surface morphology and chemical composition obtained using surface analytical methods, including atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). In particular, we report on PDMS surfaces modified with a series of perfluoroalkylsilanes of varying perfluorinated chain length, in order to determine the effect of surface coverage and morphology on the ζ-potential. The results are discussed in the context of previous reports on the structure and solvation of perfluoroalkyl surfaces; the effects of fluid slip and surface inhomogeneity on ζ-potential measurements; and the adsorption of solution counterions on surface charge.

2. Experimental

Details of the PDMS device fabrication and ζ-potential measurements have been presented elsewhere [20]. Briefly, Sylgard 184 PDMS prepolymer and cross-linker (Dow Corning, Midland, MI, USA) were mixed in a 10:1 (w/w) ratio and degassed by a vacuum desiccator. The mixture was subsequently poured onto four petri dishes with capillary columns (164 μm o.d.) on the bottom that had been fixed in advance. After curing at 65 °C for 4 h, the PDMS layer was peeled off from the petri dishes. The patterned PDMS microfluidic substrate was then cut into channel Plates 9 cm in length by 2 cm in width. PDMS cover plates were prepared in the same manner as the channel plates, except there were no capillary columns fixed at the bottoms of the petri dishes. Inlet and outlet holes, 4 mm diameter in diameter, were drilled in each cover, separated by 8 cm.

The PDMS microfluidic channels and unpatterned covers were treated using an air plasma generator (Harrick Scientific Corporation, Ossining, NY) for 2 min (10.2 W, 10 MHz rf level at 80 mTorr). Previous characterization of such surfaces using a combination of XPS, AFM, contact angle and zeta potential measurements [15,18,20] has demonstrated that under these conditions the PDMS surface becomes saturated with SiOH sites. To fluorinate the PDMS surfaces, the four freshly-oxidized PDMS substrates and covers were each immersed in one of a 10 mmol/L solution of 1H,1H,2H,2H-perfluorohexyltriethoxy-silane (PF-6), 1H,1H,2H,2H-Perfluorooctyltriethoxysilane (PF-8), 1H,1H,2H,2H-perfluoro-decyltriethoxysilane (PF-10), 1H,1H,2H,2H-perfluorododecyltriethoxysilane (PF-12) or 1H,1H,2H,2H-perfluorotetradecyltriethoxysilane (PF-14) (SynQuest Laboratories, Inc.), which had been dissolved in either toluene or perfluorodecalin (PFD) for 15 h. The solution temperature was 20 °C. After modification, the samples were washed with methanol and dried in air.

The measurement of the ζ-potential of the micro channels was performed using current-time monitoring [19] with a microfluidic tool kit (Micralyne, Edmonton, Alberta). The microchannels were first filled with a high-ionic-strength phosphate buffer solution (30 mmol L^{-1}). Then the inlet buffer reservoir 1 (see schematic, Fig. 1) was emptied and filled with a lower ionic-strength phosphate buffer solution (28.5 mmol L^{-1}). Platinum electrodes were immediately placed in the inlet and outlet buffer reservoirs. Finally, an electric field (strength $E = 0.5$ kV) was applied and the current was monitored as a function of time.

The electroosmotic flow velocity, μ_{eo}, could be measured based on Eq. (1), in which L is the length of microfluidic channel and t is the time needed for the lower ionic strength solution to fill in whole channel (Fig. 1).

$$\mu_{eo} = \frac{L}{t} \tag{1}$$

In addition, the Smoluchowski equation

$$\mu_{eo} = \frac{\varepsilon_0 \varepsilon_\gamma \zeta}{\eta} E_Z \tag{2}$$

may be used to determine the zeta potential, ζ, at the interface, where E_z is the applied electric field strength, η is the solution viscosity, ε_o is the electrical permittivity of vacuum, and ε_r is the dielectric constant for water. In this work, the measured value of the ζ-potential was repeated three times for each data point. It was repeatable within ±5%.

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition of unmodified, oxidized and fluorinated PDMS. XPS measurements were performed using a Thermo Microlab 310F ultrahigh vacuum (UHV) surface analysis instrument using Al Kα X-rays (1486.6 eV) at 15 kV anode potential and 20 mA emission current with a surface/detector take off angle of 75°. The binding energy of all spectra were calibrated to the C 1s line at 285.0 eV. A Shirley background subtraction algorithm was used as the background subtraction method for all peaks. The Powell peak-fitting algorithm was used, with peak areas normalized between different elements using the relative XPS sensitivity factors of Scofield [21]. In cases where absolute peak intensities for a single element were compared between different samples we took care to ensure a standard sample size and orientation with respect to X-ray source and detector within the analysis chamber. Calibration of our system using Au thiol SAMs of known surface concentration has shown that peak areas are reproducible within ± 5% between sample runs. The PDMS samples used in XPS analyses were prepared using the same prepolymer, curing agent and modification processes noted above.

The AFM images were acquired in the tapping mode of the Veeco multimode microscope equipped with a Nanoscope IIIa controller. The tips used were standard Si_3N_4 tips (a radius of curvature typically less than 5 nm) with a resonance frequency of 100 kHz. Height and phase-shift data were recorded simultaneously, although only the height mode images are shown here. Images were recorded at scan rates of 1–2 Hz.

Contact angles were measured using a VCA optima (AST Products, Inc.) system. A 1 μL drop of deionized water was placed on the substrate, and static contact angles were measured on both sides of the drop. The contact angles were measured at least three distinct spots on each sample, and the reported values represent the average and standard deviation of the measurements.

3. Results and discussion

To ensure reproducibility and maximum coverage of the perfluoroalkyl layer on PDMS, a series of experiments were carried out in order to ascertain the effect of several variables on the surface modification process. In addition to the identity of the perfluorinated species itself (i.e. chain length), these included the plasma