Journal of Metals, Materials and Minerals. Vol.16 No.2 pp.47-52, 2006

pH Dependant Coating for Microfluidics Devices

Luxsana LIMSAVARN[1], Chatr PANITHITONGWNT[1],
Prangthong THONGKORN[1], Stephan T. DUBAS[2*]

[1] Department of Chemistry, Faculty of Science,
Chulalongkorn University, Bangkok, Thailand
[2] Metallurgy and Materials Science Research Institute,
Chulalongkorn University, Bangkok, Thailand

Received Oct. 12, 2006
Accepted Nov. 6, 2006

Abstract

The layer-by-layer technique was used to coat the channels of PDMS microfluidics devices. The coating was based on the sequential deposition of polydiallyldimethylammonium chloride (PDADMAC) with a copolymer of polystyrene sulfonate and maleic acid (CoPSS-Maleic) into polyelectrolyte multilayer (PEM). The possible deposition of PEM coating on PDMS was confirm by contact angle which showed the clear transformation of the PDMS surface from hydrophobic to hydrophilic. The later deposition of the PEM coating inside the micro-channels was confirmed by change in electroosmotic flow direction (EOF) and intensity as a function of the number of deposited layers. The EOF measurements revealed that after the deposition of only 2 layers, the flow direction and intensity already reached its maximum value oscillating between $-2.5\text{x}10^{-4}$ cm^2/V.S and $4.1\text{x}10^{-4}$ cm^2/V.S as a function of the positive or negative top layers of the coating. The changes in EOF value as a function the pH in the solution were also investigated. The intensity of the electroosmotic flow was influenced by the pH of the solution, which affects the charge density at the surface of the PEM coating. This property can be used to tune the separation resolution, which is the missing parameter in uncoated PDMS chip.

Key words : Microfluidics, polyelectrolyte multilayers, EOF, PDMS.

Introduction

For the preparation of microfluidics devices, several polymers such as polydimethylsiloxane (PDMS), poly(methyl methacrylate) (PMMA) and polycarbonate (PC) have been uses as base materials for the chip fabrication. Among all, PDMS has received the most attentions mainly due to its ease of preparation, low cost, good transparency and non-toxicity. However, PDMS based microfluidic devices showed some defects that need to be overcome such as the generation of air bubble in channels, and the unstable electroosmotic flow (EOF). Foremost among PDMS's disadvantages are its extreme hydrophobicity and the non-specific absorption of some hydrophobic compounds on the PDMS surface during using. These problems have been recognized as a major challenge toward the development of many applications including protein analysis.(1)

A number of efforts have been made to improve the EOF stability, control the intensity of the EOF, render the surface more hydrophilic and eliminate the non-specific adsorption. Most of these concerns, the use of chemical modification procedures including exposure to energy sources such as plasma.(2,3) or UV light.(4-6) radiation induced graft polymerization.(7) cerium (IV) catalysis(8) silanization(9) atom-transfer radical polymerization(10) or the sol-gel method.(11) The dynamic modification of the PDMS surface with surfactants such as tetrabutylammoniumchloride (TABCl), sodium dodecyl sulfate(12) Brij-35(13) and amine-containing polymer(14) was used to control EOF and reduce adsorption of the analytes as well but with moderate success.

Few years ago, the polyelectrolyte multilayers (PEMs) technique was introduced as an interesting alternative for the surface modification of plastic microfluidic devices as a surface modification method to control the surface chemistry of plastic microfluidic devices for reproducible and controllable separations.(15-18) Assembled by taking advantage of the electrostatic interaction between oppositely charged polyelectrolytes and deposited in a sequential fashion,

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Corresponding author. Tel. +66-2218-4234

Liu et al. employed the PEM technique to modify the surface of PDMS/glass microchannel with a bi-layer film of polybrene (PB) and dextran sulfate (DS), which appeared to be stable for more than 50 runs and provided a nearly pH-independent EOF between pH 5 and 10.(19)

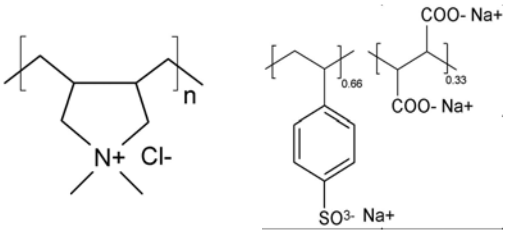
In CE separation, in order to improve the efficiency of the system, it is necessary to manipulate various parameters such as the electrophoretic mobility of the analyte or the electroosmotic flow in the separation channel. With uncoated PDMS, it is relatively difficult to adjust (instead of control) the EOF because the the charge of channel PDMS is fixed by the chemistry of the material used. The utilization of the PEM assembly technique has been reported by Zje *et al.* for glass capillary used in capillary electrophoresis. In their system a copolymer of polydiallyldimethylammonium chloride and poly acrylate was used as a constituent of the PEM, which provided complete reversal of the EOF upon pH change on the solution.(20)

In the present article, we investigated the effect of the coated PEM thin film on the EOF reversal during the PEM assembly as well as EOF changes as a function of the pH of the solution. The build up of the PEM on PDMS was confirmed by contact angle measurements.

Experimental

Chemicals

Sylgard 184 (PDMS) was from Dow Corning (Midland, MI, USA). Cationic polyelectrolyte (polydiallyldimethylammonium chloride, PDADMAC) (MW of 400,000-500,000) and anionic polyelectrolytes (copolymer of polystyrene sulfonate and maleic acid, CoPSS-Maleic) (MW of 20,000) were purchased from Aldirch. Na_2HPO_4, KH_2PO_4, $Na_3PO_4 \bullet 12\ H_2O$, CH_3COONa, $Na_2B_2O_7 \bullet 10\ H_2O$, NaOH and NaCl were purchased from Carlo Erba. Methanol (HPLC grade), phosphoric acid and acetic acid (glacial) were purchased from Merck. All polyelectrolyte solutions were prepared in 1 mM NaCl. All solutions were filtered through a 0.2 μm Nylon filter, 1.3 i.d. (Chrome Tech). All chemicals are analytical grade and used without further purification. All solutions were prepared with water purified with a Milli-Q water purification system (Nihon Millipore, Tokyo, Japan) for the EOF studies and with double distilled water for the contact angle studies.



PDADMAC CoPSS-Maleic

Figure 1. Chemical structure of polydiallyl-dimethy-lammonium chloride, PDADMAC and polystyrene sulfonate, coPSS-maleic

PDMS preparation

The PDMS oligomer was mixed with the curing agent in the ratio of 10 :1.1 to form a PDMS prepolymer mixture and degassed in a vacuum. The mixture was cured against either the bare silicon wafer that had been cleaned with the piranha solution (H_2SO_4:H_2O_2, 2:1), water and methanol and dried with a nitrogen stream for contact angle measurement. For EOF measurement, the degassed prepolymer mixture was poured onto a silicon master which has the pattern that has been cleaned sequentially with water and methanol and air dry. After at least 2 hours of curing at 65°C, the PDMS replica was peeled from the mold. The cured PDMS sheets were cleaned with methanol and water, and then dried in the air. Buffer reservoirs were then opened with a hole puncher. Bare PDMS replicas were formed by casting the PDMS mixture on a clean dry silicon wafer.

PEM buildup

Flat PDMS substrates are cut to 2 cm2 rectangular pieces. Before beginning the PEM deposition, PDMS piece was cleaned with methanol. For the PEM thin film buildup, the substrate was first immersed for 5 min in a solution containing 1 mM of PDAD in 1 MM sodium chloride. The sample was then rinsed three times in de-ionized water for 1 min. The purpose of the rinse bath is to remove the excess and loosely bound polyelectrolytes from the surface. These steps resulted in the deposition of a thin layer of PDAD, which had for effect to reverse the charge at the surface of the sample from negative to positive. The surface with the PDAD top layer was then immerse for 5 min in a solution containing 1 mM of coPSS-maleic and 1 MM sodium chloride followed by three rinses in water. These steps resulted in the deposition of a bi-layer of PDAD–coPSS-maleic and were repeated as for 10 layers. A homemade robot was used to improve reproducibility and to allow the facile deposition. All pieces were spun with a homemade sample holder while in solution to accelerate the deposition process and render the PEM more uniform.

Contact angle measurement

The water contact angles were measured on non-coated PDMS and coated PDMS for every deposited layer. Contact angel measurements were carried out using an contact angle machine, with each data point representing an average of three 10 μL droplets each measured three times, for a total of nine measurements.

Coating procedure and electroosmotic flow measurements

Reversible sealing involved thoroughly rinsing a PDMS replica and a blank PDMS piece with methanol and bringing the two surfaces into contact with one another prior to drying. The assembled microchip was then dried in an oven at 65°C for 15 minutes.(19) Electroosmotic studies were done on a PDMS/PDMS microchip. The single straight channel (3.6-3.8 cm long, see Figure 2) was used in this study, which the width and the depth of the channel are 50 and 50 μm, respectively.

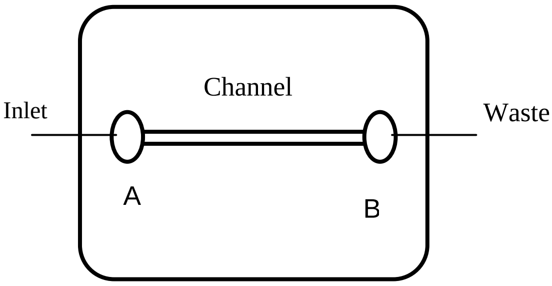


Figure 2. schematic of the microchip used for the current monitoring experiments. Channel: 50 μm width, 50 μm deep

PDMS/PDMS channels modification

After sealing, the separation channel was rinsed with methanol and ultrapure water, respectively for 5 min each using vacuum pump. Then 100 μL of 0.1 M NaOH was pumped through the channel. The solution sit inside the channel for 15 min then rinsed with water for 5 min. Once preconditioned, the channel was filled with 50 μL of 10 mM PDADMAC in 1 M NaCl solution and allowed to set for 15 minute followed by pumping water for 5 min (rinsing step). Coating anionic polyelectrolyte is performed in the same manner. After each layer coating, the EOF measurements were performed. All filling steps were performed by applying a vacuum pump to the buffer waste reservoir with the other reservoir filled with the respective rinsing solution. Up to 10 layers were deposited for EOF measurement. 1 mM PDADMAC and PSS solutions were used in the optimization coating study.

Measurement of EOF

The EOF was measured by a current-monitoring method.(21) The pH 7 phosphate buffer with a concentration of 10 and 9 mM were used as running buffer solutions for current monitoring technique. The procedures for this are described briefly below. For the uncoated surface and PSS (anionic) coating microchannel, 10 mM buffer was pumped through the separation channel via a vacuum pump for at least 5 min. Rinse both reservoirs with water. After the A reservoir was filled with 70 μL of 9 mM solution, the B reservoir was replaced with a 70 μL of 10 mM buffer solution. The A reservoir was connected to a high-voltage power supply through a platinum electrode, while the B reservoir was grounded. This setup was used for all EOF experiments. The constant voltages applied to A and B reservoirs were set to 600 V. After the current reached a plateau, the chip was rotated. The B reservoir was refilled with concentrated buffer, then the potential was reapplied. The time required for the current plateau was indicative of the buffer filling the separation channel. The A reservoir was then refilled with 9 mM buffer and the above procedure repeated. Six consecutive measurements were obtained for each experiment. For reversed EOF measurement (cationic polyelectrolyte coated surface), the A reservoir, first, was filled with 10 mM, while B reservoir was filled with 9 mM. The value of EOF was calculated using the following equation:

$$\mathrm{EOF} = L/tV \qquad \text{(eq 1)}$$

where L is the length of the separation channel, t is the time between the stable current values and V is the applied voltage (600 V). Calculate for EOF and %RSD.

Results and Discussion

Monitoring of the polyelectrolyte multilayers coating on PDMS by contact angle measurements

Using the contact angle technique we confirmed the possible coating of a PDMS substrate with the PEM technique. The hydrophobic nature of the PDMS materials can be rendered hydrophilic by deposition of polyelectrolyte multilayers. By recording the change in contact angle as a function of the number of layers we see that after 6 layers the hydrophobic nature of the PDMS decreased and we can observe oscillation of the contact angle as a function of the polyelectrolyte top layer. We suggest that similar behavior and coating would occur in the microfluidics channels of the separation device. The successive deposition of PDADMAC and coPSS-maleic lead to such an oscillation in contact angle due to the difference in hydrophobicity provided by the dimethyl group of the PDADMAC and the more hydrophilic sulfonate and carboxylic group from the coPSS-maleic. For the first few layers, the slow change in contact angles is probably due to a slow nucleation growth of the PEM coating on the hydrophobic PDMS surface. Nearly 3 coating cycles are required to allow the formation of a thin film at the surface of the PDMS surface leading to steady oscillation in contact angle.

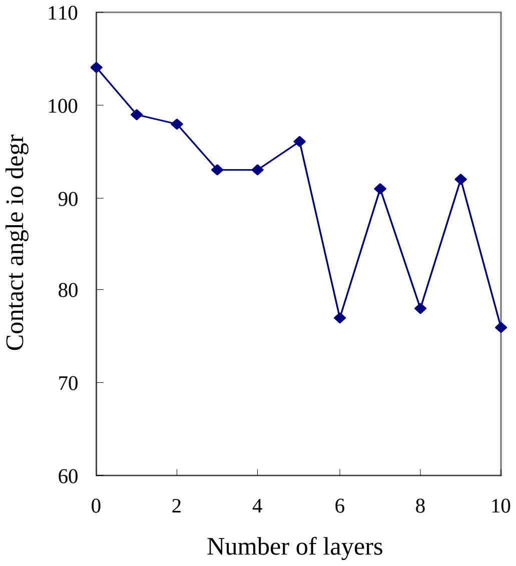


Figure 3. Contact angle as a function of the number of PDADMAC-CoPSS-Maleic layers.

Dynamic coating of PDMS/PDMS microchips using polyelectrolyte multilayers coating and the change in EOF mobility

When applying the same deposition technique to the microfluidics channel we can no longer measure the contact angle because the channel as a dimension of 50 micron which is of course too small for contact angle measurements. Instead we can measure the EOF intensity as a function of the number of deposited layers. The EOF is function of the surface charge density present on the channel wall and will be influenced by the PEM coating. As can be seen in Figure 4, the expected reversal of the EOF as a function of the deposited layers with the odd layers being with PDADMAC on top and even layers with coPSS-maleic on top.(15) After only 2 layers, the EOF values for the PDADMAC has reached its maximum values of $-2.5x10^{-4}$ cm^2/V.S, while coPSS-maleic required about 7 layers to reach its maximum value ($41x10^{-4}$ cm^2/V.S). The differences in their EOF values can be rationalized by the lower charge density of the PDADMAC monomer when compared with the coPSS-maleic. Moreover, the PDADMAC positive charge is somewhat screen by the two-methyl groups from each monomer, which tends to reduce the ion interaction in the double layer near the micro-channel wall and therefore reduces the EOF absolute value.

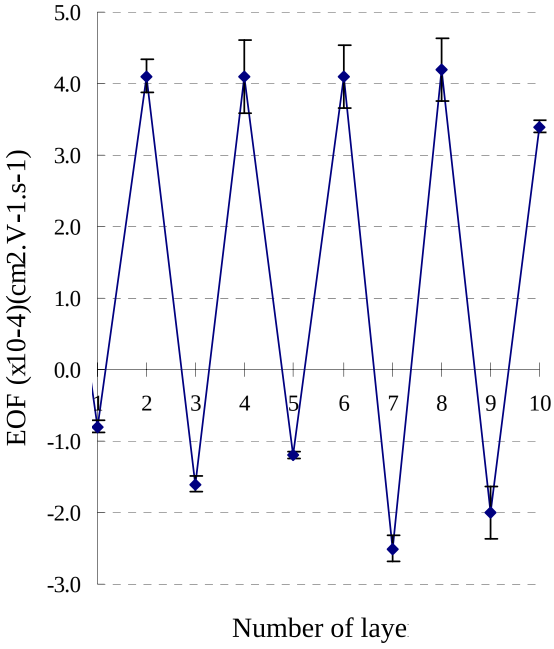


Figure 4. EOF reversal as a function of the number of PDADMAC-CoPSS-Maleic layers.

Effect of the pH on the EOF

The effect of the pH on the EOF was investigated for pH value ranging from acidic to basic (pH = 3, 7, 9 and 11.2). The effect of the pH on the film is expected to modify the charge density present at the film surface. The charge density is function of the switching, as a function of pH, of the carboxylic / carboxylate functional groups from the coPSS-maleic. While the sulfonate groups are known to remain ionized from pH 1 to 14, the weak carboxylic acid with a pKa around 4.5 can be ionized giving COO- species in more alkaline medium. As a result of this switching due to pH change and surface charge density, change in EOF can be observed. The EOF is seen (Figure 5) increasing from a value of 2.9 to 4.8 with increasing pH from 3 to 11.2. The possibility to control the EOF is a clear advantage in separation, since it can improve the separation power of the microfluidics device. It is also interesting to note the excellent EOF value even in acidic solution at pH 3, which is usually not possible when using traditional PDMS microchip.

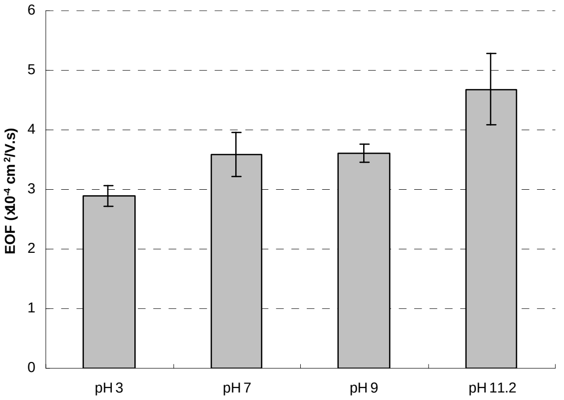


Figure 5. The electroosmotic mobility as a function of the pH value of the separation solution.

Conclusions

The layer-by-layer deposition of polyelectrolytes multilayers was used for the formation of hydrophilic coatings inside microfluidics channels. The EOF reversal data and contact angle changes were used to evaluate the effectiveness of this coating. Good coating is obtained after few layers as confirmed by steady reversal of the EOF and contact angle as a function of the layer deposited. Furthermore, the EOF can be controlled by adjusting the pH of the solution which affects the charge density of the PEM coating in the microfluidics channel. The use of pH dependant copolymer is an interesting feature of this coating which can provide variety values of EOF in a wide range of pH. These coatings might be useful in the future design of microfluidics devices where EOF control is required.

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