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Polyelectrolyte multilayers coating for organic solvent resistant microfluidic chips

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ABSTRACT

The layer-by-layer (LbL) deposition technique was used to coat and protect poly(methyl methacrylate) (PMMA) and poly(dimethylsiloxane) (PDMS) substrate from organic solvent. PMMA and PDMS substrates were protected by polyelectrolyte multilayers (PEM) thin films of either poly(diallydimethiyl ammonium chloride) and Poly(styrene sulfonate) PDADMAC/PSS or chitosan/alginate. The PEM depositited on the PMMA and PDMS substrates improved the organic solvent resistance with the best results obtained from the chitosan/alginate over the PDADMAC/PSS pair. The more hydrophilic character of the chitosan/alginate and the PDADMAC/PSS film caused a significant decreasing rate of organic solvent pentration into the PMMA substrate which retain transparent optical properties for up to 30 dipping in acetonitrile. A 20 layers chitosan alginate film also decreased PDMS substrate swelling when exposed to chloroform vapor. The PEMs coating could protect the PMMA and PDMS sample against organic solvent and vapor which could make them useful in microfluidic systems even in agressive environment.

1. Introduction

Microfluidic technology revolutionized the field of analytical chemistry by providing high resolution analysis with low reagent volume, sample consumption and cost. [1–5] Typically, these devices are fabricated using glass, polymeric materials, elastomers, or a combination of these. [6–10] great effort is made to make develop microfluidic devices for bioanalysis, of DNA, proteins in aqueous and organic medium. [11–14] While the utilisation of microfluidic devices with water is not a poblem, organic solvent cause loss of tranparency of substrates such as PMMA or swelling of PDMS based microchip. [11,15] In this configuration the low cost polymeric materials cannot be used unless a solution is found to protect the polymer from the organic solvent. Coatings from polyelectrolytes which are soluble in water but not in organic solvent due to their polyanionic or polycationic nature could be a good solution to protect polymeric surface from non-polar solvents. These thins polymer films can be built using the layer-by-layer deposition approach proposed by Decher in the early 90's. [16] The layer-by-layer assembly is described as sequential adsorption of positive or negative charged species by sequential dipping a substrate into in each solution. Bruening et al. have prepared PEM film on filters which were able to separated water from ethanol. [17] Their work showed that the electrostatic environment found inside the PEM film had a low affinity with non-polar solvents and only let water and ions to permeate through the film. Based on this hypothesis, PEM thin films were coated onto PMMA or PDMS and respectively exposed to acetonitrile and chloroform vapor. Our hypothesis was that the coating would repel the solvent and protect the substrates. If successful, no change in transparency of the PMMA sample and no swelling of the PDMS pieces would be observed. Two types of PEM films based on the sequential adsorption of PDADMAC/PSS and chitosan/alginate were tested. UV–Vis spectroscopy was used to monitor the level of transmitted light trough the PMMA sample when exposed to acetonitrile. Improvement of the compatibility if the polymeric microchip with non-polar solvent are of great interest for the development of hybrid chips that can be used in various environment and for various types of applications requiring either water or organic compatibility.

2. Experimental procedure

2.1. Chemicals

Chitosan was purchased from A.N. (aquatic nutrition lab) Ltd., Thailand. Alginate, poly(diallyldimethylammoniumchloride) (PDADMAC, medium molecular weight, 20 wt.% in water, typical Mw = 200,000–350,000), poly(sodium 4-styrene sulfonate) (PSS, typical Mw = 70,000) were purchased fromAldrich, Thailand. Sodium chloride A.R. grad was purchased from Labscan Asia Co., Ltd., Thailand. Acetonitrile was purchased from Merck, Thailand. Chloroform A.R. grad was purchased from CARLO ERBA, Thailand. PDMS base and curing agent (Sylgard 184 elastomer kit) was purchased from Dow

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Corning, Thailand. PMMA sheets were purchased from Sumipex Co., Ltd. Thailand. All chemicals and solvents were used as received without any further purification. Double distilled water was used in all experiments.

2.2. Coating of the PMMA with PEM thin films

1 mm thick PMMA sample were cut into plates of 2.5 × 7.5 cm which and coated using the layer by layer deposition process described elsewhere. chitosan/alginate and PDADMAC/PSS polyelectrolyte pairs had a monomer concentration of 5 mM and a pH value of 5.5. The ionic strength of the polyelectrolyte solutions was adjusted to 1 M NaCl. The substrates were dipped for 2 min in each polyelectrolytes solution followed by three rinses in water for 1 min. These steps were repeated until the desired number of layers was obtained.

The thickness of the film was measured by atomic force microscope (Veeco, Multimode used in tapping with silicon tip) by doing a scratch with a soft tip and measuring the step height.

2.3. Testing of the solvent resistance

The percent transmittance of the PMMA sample was measured using fiber-optic spectrophotometer (ocean optic red tide USB 650). The coated PMMA samples with either the chitosan/alginate or the PDADMAC/PSS PEM film were immersed into acetonitrile for up to 60 min. PMMA was then removed from acetonitrile solution and the percent transmittance of PMMA was record at 550 nm every 2 min. To investigate the solvent compatibility of PDMS, pieces of PDMS (3 cm × 3 cm × 0.3 cm) were used for swelling measurement. The mass of bare PDMS and chitosan/alginate coated PDMS were measured while exposed to chloroform vapor for 120 min.

3. Results and discussion

In order to protect the PMMA surface from organic solvent, polyelectrolyte multilayers are used here as a hydrophilic barrier. Because of their ionic structures, these coatings tend to repel hydrophobic solvent and here, two types of PEM thin films, PDADMAC/PSS and chitosan/alginate, were tested. The choice of these two types of PEM was driven by the fact that the first PDADMAC/PSS pair is made of synthetic polymer commonly used in PEM studies while chitosan/alginate are bio-polymer. [18,19] The ionic character as well as the presence of a large amount of hydroxyl groups along the biopolymer repeat unit was hypothesized to provide a stronger hydrophilic character and therefore better protection against non-polar solvent when compare the standard PDADMAC/PSS pair. The layer-by-layer assembly of both polyelectrolytes pair, PDADMAC/PSS and chitosan/alginate, has been reported elsewhere and is due to the electrostatic interaction between the oppositely charged polyelectrolytes. [20,21] A pH value of 5.5 was used for chitosan–alginate as it represents the condition under which both polyelectrolytes are well ionized and near their respective pKa. The pH of the PDADMAC/PSS pair was not adjusted because these two polyelectrolytes are pH independent and fully ionized for pH values between 1 and 14. The thickness of the prepared film from both PDADMAC/PSS and chitosan/alginate after 20 layers was measured to be 400 nm and 100 nm respectively. The effect of both PEM coatings was first tested by dipping PMMA slides in acetonitrile and recording the change in transparency as a function of time for each coating. Using UV–Vis spectroscopy, the loss of transparency as a result of the solvent diffusion can be characterized for each coating when compared with the bare PMMA sample. From Fig. 1 it can be seen that the percent transmission through the bare PMMA decreases rapidly as a result of the solvent diffusion which leads to swelling and produce an opaque PMMA film. In contrast, when increasing the number of deposited layers for both PDADMAC/PSS (Fig. 1-A) or chitosan/alginate (Fig. 1-B) films, the transparency is maintained for 25 to 30 min respectively. It can be seen that for both PEM coating, the solvent protection provided when using 6 layers is poor and is due to the incomplete coating of the PMMA surface. This can be explained by the low charge density of PMMA making it difficult for the polyelectrolytes to anchor on the surface. Nevertheless when 20 layers of chitosan–alginate or PDADMAC/PSS were deposited, the chitosan/alginate pair performed better and pictures of the different PMMA samples after 15 min are shown in Fig. 2. It can be seen that the bare PMMA is totally opaque, the PDADMAC/PSS coated is starting to become opaque but the chitosan/alginate sample remains transparent. Interestingly, although the chitosan/alginate film had a thickness of about a quarter of the PDADMAC/PSS film, its resistance to the solvent was found to be better. This confirms the superior solvent protection provided by the chitosan/alginate films.

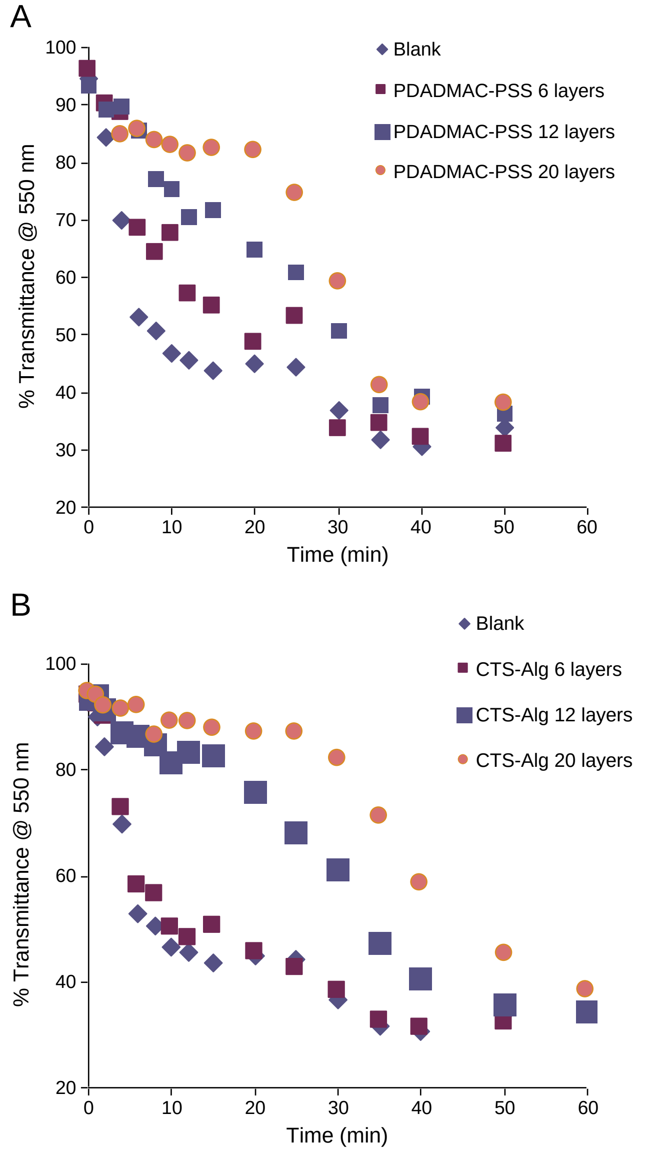

Fig. 1. Percent transmittance of PMMA substrates coated with 0, 6, 12 and 20 layers of PDADMAC-PSS(A) and chitosan–alginate(B) when dipped in acetonitrile as a function of time.

In contrast, the PDMS sample remained transparent when dipped in organic solvent due to their cross linked nature. The effect of solvent interaction is then limited to swelling which leads to loss of contact between the microchip part and leakage. Therefore we chose to observe the change in weight as a result of solvent adsorption as