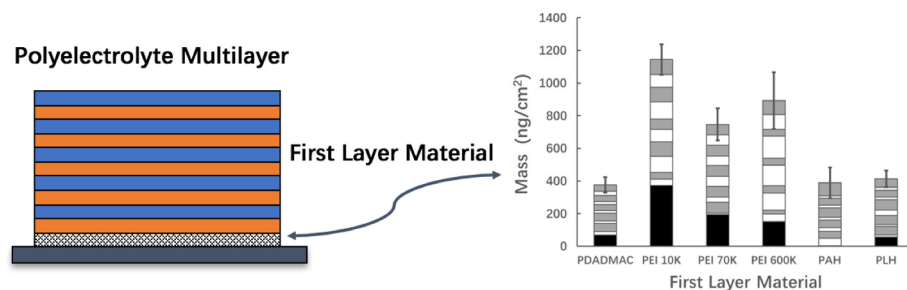


Regular Article

The Princess and the Pea Effect: Influence of the first layer on polyelectrolyte multilayer assembly and properties

Xuejian Lyu^a, Amy M. Peterson^{a,b,*}^a Department of Mechanical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609, United States^b Department of Chemical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609, United States

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 February 2017

Revised 26 April 2017

Accepted 27 April 2017

Available online 29 April 2017

Keywords:

Polyelectrolyte multilayer
 Polymer coatings
 Quartz crystal microbalance
 Ellipsometry
 Atomic force microscopy
 Surface chemistry

ABSTRACT

In many applications of polyelectrolyte multilayers (PEMs), a base polycation layer is adsorbed to promote adhesion of the PEM to the substrate. In this report, the effect of the first polyelectrolyte adsorbed in a PEM was investigated by assembling PEMs with first layer polycations of different chemistries and molecular weights. In this study, quartz crystal microbalance with dissipation monitoring (QCM-D) was used to monitor the PEM assembly process. First layer choice affects the total mass accumulation of the PEM as well as the stoichiometry of the PEM, although linear growth was observed in all cases. PEM thickness was also affected by first layer choice, although not consistent with changes in mass. Combined with the stoichiometry results, these findings indicate that the structure of a PEM is fundamentally different depending on first layer chemistry and molecular weight. PEM topography is also affected by first layer choice. Selection of appropriate first layer material is therefore an important consideration in the design of a PEM, and changing first layer material may be a facile way to tailor the structure and properties of PEMs.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

PEMs are polymeric structures that are prepared via layer-by-layer assembly of polycations and polyanions on a substrate. This technique, which was first described in the early 1990s, provides

an approach to assemble multi-functional polymer structures [1–4]. PEM coatings have been used for obtaining superhydrophobic [5] and nano-patterned surfaces [6,7], as well as corrosion inhibition [8] and self-healing [9]. One important application of PEMs is controlled release of biologically relevant molecules from PEM coatings or capsules [10–15].

Although PEMs have demonstrated uses in a wide range of applications, controlling PEM properties is challenging because of

* Corresponding author at: Department of Chemical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609, United States.

E-mail address: ampeterson@wpi.edu (A.M. Peterson).

their sensitivity to many material and processing parameters. As is described below, the structure and properties of a PEM are dependent upon many material and assembly parameters including polyelectrolyte molecular weight [16], pH [17], and salt concentration [18–20].

Polyelectrolyte molecular weight has been shown to affect PEM assembly. In work from Sui et al., lower molecular weight poly(sodium 4-styrenesulfonate) (PSS) stripped off polyanions instead of adsorbing to the PEM during the assembly step [16]. Greater stripping was observed with increasing salt concentration, as salt increases polyelectrolyte mobility. Lower molecular weight poly(methacrylic acid) (PMAA) within a PMAA/poly-L-histidine PEM was shown to reduce the amount of burst release and increase sustained release of negatively charged model polypeptides [21].

Assembly pH is a simple parameter to adjust that changes weak polyelectrolyte solution conformation, leading to differences in the resulting PEMs. Shiratori and Rubner observed that the thickness of weak polyelectrolyte PEMs decrease with increasing assembly pH [17]. We previously reported that assembly pH affects surface energy and the release rate of bone morphogenetic protein 2 (BMP2) [12], with the greatest cumulative BMP2 release occurring from PEMs assembled at pH = 4 and lowest cumulative release at pH = 6–7. Total surface energy decreased with increase of assembly pH. However, statistically significant changes in roughness and peak-valley height were not observed in these PEMs, which all used BMP2 as the first layer.

Salt concentration, both as an assembly condition and in a post-assembly annealing, can also affect PEM surface morphology. Interdiffusion in PEMs assembled from poly(diallyldimethylammonium chloride) (PDADMAC) and PSS was enhanced after annealing in a salt solution [18]. PEMs assembled from PDADMAC and PSS solutions with high salt concentrations exhibited greater surface roughness as compared to PEMs assembled under low salt concentration conditions [20].

While PEM properties can be modulated by changing assembly conditions and materials, the internal structure of PEMs and how this structure affects bulk material properties are still not fully understood. Within a PEM, electrostatic interactions between oppositely charged polyelectrolytes lead to interpolymer ionic condensation. Hydrogen bonding, van der Waals forces, hydrophobic interactions and dipole interactions are non-Coulombic interactions that are also involved in their assembly [22,23]. Additionally, the relative rigidity and flexibility of polyelectrolytes affects interdiffusion [24]. All of these interactions will affect the assembly process and internal structure of the final PEM film.

Buron et al. demonstrated that different functionalization of a substrate can dramatically change PEM structure and properties [25]. The density and distribution of functional groups on a substrate affect initial polyelectrolyte adsorption and thus influence subsequent polyelectrolyte adsorption and the final PEM structure. Precursor layer surface charge has been shown to affect PEM assembly [26]. Peng et al. used four bilayers of PEI/PSS as the precursor layer and the surface charge could be tuned with assembly pH. By tuning the surface charge of precursor layer from negative to positive, the following layers will have a slower growth rate at the initial state. The substrate has also been shown to affect polyelectrolyte adsorption [27]. At the initial adsorption stage, polyelectrolytes tend to form islands if there are locations with a high concentration of local charges like scratches, holes, edges, and foreign particles on the substrate surface. Additionally, a PEI anchoring layer has been reported to enhance PEM film amount adsorbed, regardless of substrate material and heterogeneity [28,29]. It was also shown that PEMs deposited from different salt concentration solutions will have different surface wetting ability, and tend to be independent of substrate material after a certain layer number was reached [30].

The first layer of a PEM functions as a contact layer between the substrate and the rest of the PEM film; thus, the composition of the first layer may have an impact on the properties of the entire film. Peterson et al. reported a change of surface roughness when poly-L-histidine hydrochloride (PLH) was used as the first layer material instead of BMP2 in PEMs assembled from poly(methacrylic acid) (PMAA) and PLH [13]. Interestingly, differences in pre-osteoblast proliferation and alkaline phosphatase (ALP) enzyme activity, a marker of osteoblastic differentiation, were also observed that were not consistent with BMP2 release, i.e. cells on some of the BMP2 eluting PEMs exhibited less ALP enzyme activity than non-BMP2 eluting PEMs. These unexpected results highlight the importance of surface topography on cell fate, and also suggest that changes in the first layer of a PEM could affect surface topography, and potentially other surface properties.

In this study, we explore the role of first layer material selection on PEM assembly, structure and a range of PEM properties. First layer chemistry and molecular weight is shown to affect PEM mass, stoichiometry, thickness, roughness, and water contact angle. These results are discussed within the context of the effect of first layer material selection on PEMs structure and properties and mechanisms are proposed. This is the first time quartz crystal microbalance with dissipation monitoring (QCM-D) has been applied to study the influence of first layer material on PEM assembly. Using QCM-D, mass accumulation was tracked during assembly process, and it was also possible to study the adsorption behavior of PSS and PDADMAC separately.

2. Experimental

2.1. Materials

Polyethylenimine (PEI 600K, branched, M_r 600,000–1,000,000), Poly(allylamine hydrochloride) (PAH, M_w ~17,500), PDADMAC (M_w 100,000–200,000, 20 wt.% in water), PSS (M_w ~200,000, 30 wt.% in water) and PLH (molecular weight \geq 5000) were purchased from Sigma-Aldrich. Polyethylenimines (PEI 10K, branched, molecular weight 10,000, and PEI 70K, branched, molecular weight 70,000) were purchased from Alfa-Aesar. Polyethylenimines (PEI Linear, molecular weight ~25,000) was purchased from Polysciences. All chemicals were used without additional modification.

2.2. Polyelectrolyte multilayer preparation

PEMs were prepared on gold substrates (Q-Sense gold-coated sensors, QSX 301, and gold-coated quartz, purchased from PHASIS). The QSX 301 sensor is comprised of a thin quartz disc coated with a 100 nm thick gold layer. Quartz substrates were coated with 100 nm of gold to maintain the same structure and properties as the QSX 301 sensor, while providing the necessary thicker quartz substrate for ellipsometry. PEIs with different molecular weights (10K, 70K and 600K), PAH, PLH, and PDADMAC were deposited as the first layers. PSS and PDADMAC were alternately deposited after the first layer. When coating PHASIS gold-coated quartz glass, each layer was prepared by immersing the substrate in a 1 mg/mL polyelectrolyte solution for 15 min followed by three rinses in 60 ml DI water for 1 min each. In total, 11 polyelectrolyte layers (5.5 bilayers) were deposited. When using Q-Sense gold sensors as the substrate, each layer was coated by flowing polyelectrolyte solutions across the sensor as described below.

2.3. QCM-D analysis

QCM-D was used to characterize the adsorption of each layer during the PEM assembly process. QCM and QCM-D are common

Download English Version:

<https://daneshyari.com/en/article/4984635>

Download Persian Version:

<https://daneshyari.com/article/4984635>

[Daneshyari.com](https://daneshyari.com)