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Journal of Membrane Science

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

Influence of polymer interdiffusion and clay concentration on gas barrier of polyelectrolyte/clay nanobrick wall quadlayer assemblies

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ARTICLE INFO

Article history:

Received 6 July 2013

Received in revised form

14 October 2013

Accepted 15 October 2013

Available online 21 October 2013

Keywords:

Layer-by-layer assembly

Gas barrier

PVAm

Ionization

Nanobrick wall

ABSTRACT

Thin film assemblies of polyvinylamine (PVAm), branched polyethylenimine (PEI), poly(acrylic acid) (PAA) and sodium montmorillonite (MMT) clay, created using the layer-by-layer assembly technique, demonstrate the influence of polymer interdiffusion and clay concentration on oxygen barrier behavior. These quadlayer (QL) assemblies can be switched from linear to exponential growth by varying the placement of PVAm and PEI layers. PEI has a much lower T_g and is better able to interdiffuse with PAA, resulting in exponential growth and greater clay deposition in each layer. When deposited on 179 μm poly(ethylene terephthalate) (PET), these 'nanobrick wall' thin films only decreased visible light transmission by 2% as the thickness increased by a factor of 10, indicating that clay platelets are highly oriented and well separated. Atomic force and transmission electron microscope images also reveal this high level of clay orientation that creates an extended gas diffusion pathway that dramatically reduces oxygen transmission rate (OTR). A 6QL PVAm-based assembly, with a thickness of 175 nm, has an OTR of 0.009 $\text{cm}^3/(\text{m}^2 \text{ day atm})$. OTR was found to be linked to both the degree of polymer interaction and clay concentration in these thin films. The desired barrier can be obtained by substituting PVAm layers for PEI. This study demonstrates a promising technique for tailoring the gas barrier of polymer/clay composite thin films that could find use in flexible electronics and food packaging.

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1. Introduction

Over the past two decades, layer-by-layer (LbL) assembly has been widely studied as a simple and versatile method to create multifunctional thin films [1–3]. By alternately depositing positively and negatively charged materials, LbL assemblies have been shown to exhibit antimicrobial [4–6], antireflection [7–9], desalination [10–12], flame resistant [13–15] and drug delivery properties [16–18]. The advantage of this technique is the precise tailorability of thin film morphology and structure through adjustment of concentration [19], pH (ionic strength) [20,21], chemistry [22], temperature [23,24], molecular weight [25,26] and deposition time [27,28] of the aqueous deposition mixtures.

In addition to the properties mentioned above, the super gas barrier exhibited by some assemblies has led to significant study [29–33]. Two approaches have been used to produce low oxygen permeability. The first is to create an extremely tortuous path by layering nanoplatelets, such as clay and graphene oxide [31,32]. The impermeable gas platelets create a tightly packed nanobrick

wall structure that significantly extends the diffusion pathway of a gas molecule. The best system to-date is a quadlayer (QL) system prepared by repeatedly depositing polyethylenimine (PEI), poly(acrylic acid) (PAA), PEI, and montmorillonite (MMT) clay [31]. In this case, a 4QL film, with a thickness of 50 nm, achieved an oxygen transmission rate of 0.005 $\text{cm}^3/(\text{m}^2 \text{ day atm})$. A second approach exploits extensive polyelectrolyte interdiffusion to obtain an exceptionally dense film [33]. The greatest oxygen barrier has been achieved with an 'exponentially growing' polyelectrolyte combination. In this case, PEI/PAA bilayers formed a 'scrambled egg' structure that enhanced thickness and densified the assembly, resulting in an OTR below 0.005 $\text{cm}^3/(\text{m}^2 \text{ day atm})$ with a thickness below 1 μm .

Further improvement in barrier performance could be achieved by combining these two concepts in a single film. For instance, weak polycations are known to have a distinct degree of ionization at a given pH and they can ionize a neighboring polyanion to a given degree, resulting a more interdiffused complex [34,35]. In the present study, cationic polyvinylamine (PVAm) and polyethylenimine and anionic poly(acrylic acid) and sodium montmorillonite were assembled as polycation/PAA/polycation/MMT quadlayers (QL). Various combinations of polycations were investigated, resulting in differences in film thickness, clay concentration (and spacing) and oxygen transmission rate. A six PVAm/PAA/PVAm/MMT

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quadlayer film has a thickness (175 nm) five times that of a 2 QL film, while its OTR is two orders of magnitude lower ($0.009 \text{ cm}^3/(\text{m}^2 \text{ day} \cdot \text{atm})$). Compared to bare PET with no thin film coating, the OTR is three orders of magnitude lower. Even more surprising was that the barrier performance of PVAm-based quadlayers is improved by simply replacing the first PVAm layer with PEI, which also reduces the overall film thickness. These transparent and flexible gas barrier films are now more tailorable, allowing a film to be designed for a specific flexible electronics or food packaging application.

2. Experimental

2.1. Materials

Branched polyethylenimine (Aldrich, St. Louis, MO) ($M_w \sim 25,000 \text{ g/mol}$) and polyvinylamine (BASF, Florham Park, NJ) ($M_w \sim 340,000 \text{ g/mol}$, >90% hydrolyzed) are cationic polymers that were dissolved into 18.2 M Ω deionized water to create independent 0.1 wt% solutions. The pH was adjusted from its unaltered value (~ 10.5 for PEI and ~ 6.8 for PVAm) to 10 by adding 1.0 M hydrochloric acid (HCl) or 1.0 M sodium hydroxide (NaOH). Titration of PVAm revealed a pKa in the range of 7.3–8.5. pH measurements for titrating 0.1 M PVAm solutions were performed using an IQ 240 pH meter (0.01 pH unit sensitivity). 10 N NaOH and HCl were used to change PVAm from its natural pH (~ 7.2) into its covalent and ionic forms (see [Supporting information](#)). Poly(acrylic acid) (Aldrich) ($M_w \sim 100,000 \text{ g/mol}$) is an anionic polymer that was prepared as a 0.2 wt% solution with 18.2 M Ω deionized water. The pH of PAA was adjusted from its unaltered value (~ 3.1) by adding 1.0 M NaOH. Anionic natural sodium montmorillonite (MMT) (trade name Cloisite Na⁺) (Southern Clay Products, Inc., Gonzales, TX) clay was prepared as a 1 wt% aqueous suspension. This suspension of high aspect ratio nanoplatelets (l/d is 80–300) [36] was used at its natural pH (~ 9.7).

2.2. Substrates

Single-side-polished (100) silicon wafers (University Wafer, South Boston, MA) were used as deposition substrates for ellipsometry and atomic force microscopy (AFM). Fused quartz slides (Structure Probe, Inc. West Chester, PA) were used for visible light transmission measurement via UV–vis spectroscopy. Both silicon wafers and quartz slides were piranha treated with a 3:1 ratio of 30% hydrogen peroxide to 99% sulfuric acid and stored in deionized water before use. *Caution: Piranha solution reacts violently with organic material and needs to be handled properly.* Prior to use, the silicon wafers were rinsed with acetone and deionized water. Poly(ethylene terephthalate) (PET) film, with a thickness of 179 μm (trade name ST505, Dupont–Teijin), was purchased from Tekra (New Berlin, WI). This film was rinsed with deionized water and methanol before use. Clean PET was then corona-treated with a BD-20C Corona Treater (Electro-Technic Products Inc., Chicago, IL). Corona treatment improves adhesion of the first polyelectrolyte layer by oxidizing the film surface [37]. Polished Ti/Au crystals, with a resonance frequency of 5 MHz, were purchased from Maxtek, Inc (Cypress, CA) and used as deposition substrates for quartz crystal microbalance (QCM) characterization.

2.3. Layer-by-layer deposition

The layer-by-layer process is shown schematically in [Fig. 1](#). A given substrate was first dipped into the polycation solution (PEI and/or PVAm) for 5 min, followed by rinsing with deionized water for 30 s and drying with a stream of filtered air. After the first positively-charged layer was adsorbed, the substrate was dipped

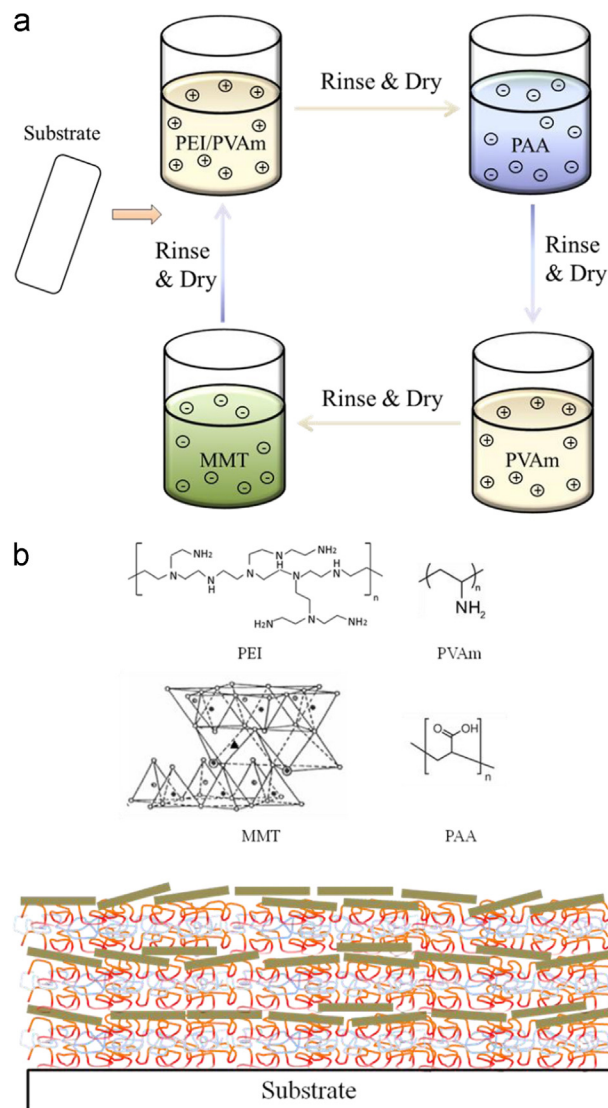


Fig. 1. (a) Schematic of the quadlayer assembly process. (b) Polyelectrolytes and clay used in the quadlayer assemblies and a cross-sectional illustration of the resultant nanobrick wall thin film. MMT structure [38]: (\blacktriangle) Al^{3+} , Mg^{2+} , $\text{Fe}^{3+/2+}$; (\circ) O^{2-} ; (\ominus) OH^- ; and (\bullet) Si^{4+} .

into PAA solution for another 5 min, followed by another rinsing and drying cycle. The substrate was then dipped into polycation and MMT solutions to form one “quadlayer”. Starting from the second deposition cycle, the remaining numbers of layers were created using 1 min dip times. This process was carried out using home-built robot systems [39,40]. The pH of PEI, PVAm or PAA is shown as a subscript next to their initials in the figures and text. For example, one quadlayer of PVAm (pH=10)/PAA (pH=4)/PVAm (pH=10)/MMT (unaltered pH of 9.7) is abbreviated as $(\text{PVAm}_{10}/\text{PAA}_4/\text{PVAm}_{10}/\text{MMT})_1$.

2.4. Film characterization

Assembly thickness on silicon wafers was measured every quadlayer with a PHE-101 Discrete Wavelength Ellipsometer (Microphotonics, Allentown, PA), using a 632.8 nm laser at an incidence angle of 65°. For the $(\text{PEI}_{10}/\text{PAA}_4/\text{PEI}_{10}/\text{MMT})$ system, 9 and 10 QL films were measured by a P-6 profilometer (KLA-Tencor, Milpitas, CA) due to their large thickness ($> 1000 \text{ nm}$). Thicknesses from 2 to 8 QLs were measured by both ellipsometer and profilometer, which showed similar values. Mass increments

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