Effect of polyelectrolyte on the barrier efficacy of layer-by-layer nanoclay coatings

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ABSTRACT

The development of effective barrier materials is becoming increasingly important, particularly as microelectronic devices and food supplies must be protected for extended periods of time from atmospheric gases and water vapor. One of the most effective, facile, eco-friendly, and inexpensive strategies introduced in this spirit is the sequential buildup of layer-by-layer (LBL) surface coatings. This technology relies on the repeated, alternating deposition of impermeable nanoclay platelets possessing a large diameter-to-thickness aspect ratio and a polyelectrolyte adhesive. Previous studies have focused extensively on the use of polycations for this purpose since they are attracted by the negative charges inherently present on the face of natural nanoclays, such as montmorillonite (MMT). In this work, we compare the barrier properties of LBL coatings prepared with a common polycation and a polyester-based polyanion, which selectively interacts with the positive charges that accumulate on the edges of nanoclay platelets. Deposition of these coatings on a hydrophobic styrenic copolymer is reported here to promote dramatic reductions in the measured permeabilities of oxygen and carbon dioxide. This study, which systematically explores the dependence of single-gas permeability on factors such as MMT suspension concentration, bilayer (BL) coating number and temperature, aims to expand the understanding of LBL coatings by also elucidating morphological considerations.

1. Introduction

Despite their generally low cost, weight and expense, polymers frequently employed to meet the demands of the packaging industry possess barrier properties that remain unacceptably low and vastly inferior to their inorganic counterparts [1,2]. For this reason, hybrid material and multistep processing strategies [3–5], resulting in single/ multiple surface coatings and bulk nanocomposite formulations, have been introduced in response to this growing need especially in the microelectronics, biomedical and food packaging industries. According to recent assessments [6], the global worth of flexible packaging is projected to reach $293 billion by 2022, and the largest share of global packaging consumption is expected to involve food and beverages (it accounted for 80% in 2014) [7]. Single surface coatings on polymer substrates can be achieved by chemical vapor deposition [2] and atomic layer deposition [4,5,8], respectively, whereas nanocomposites rely on the dispersion of nanoscale objects in a polymer matrix [9,10]. While thin solid coatings generally provide the greatest barrier efficacy (by reducing permeability by several orders of magnitude), they require

specialized chemical precursors and deposition chambers, and they are prone to defects and cracking [11–14]. In contrast, the incorporation of nanoclay in polymer nanocomposites is much less effective at decreasing gas permeability, but tends to augment mechanical properties such as modulus and toughness [8,10,15–17]. Among the tactics proposed for enhancing the barrier performance of polymer substrates, layer-by-layer (LBL) coatings [18–25] have emerged as one of the most facile, inexpensive, eco-friendly, and effective multilayer approaches capable of providing significant barrier improvement.

To be effective, hybrid organic/inorganic LBL coatings require electrostatic attraction between a polyelectrolyte and an oppositely charged, impermeable nanoparticle [25]. Repeated alternating deposition of these constituents results in a loosely arranged "brick and mortar" nanolaminate morphology, illustrated in Fig. 1. Because of their disk-like shape with a generally high diameter-to-thickness aspect ratio, natural nanoclays, such as montmorillonite (MMT), with a negative charge on each platelet face are commonly utilized in LBL coatings. As a consequence, most of the polyelectrolytes reported thus far are polycations, such as polyethyleneimine (PEI), which can
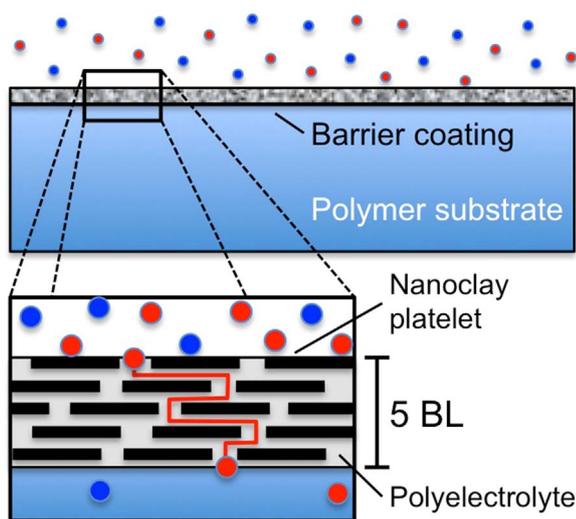
Fig. 1. Illustration of a layer-by-layer (LBL) coating applied as a gas barrier to the surface of a polymer substrate. Alternating cyclic deposition of a polyelectrolyte and nanoclay platelets generates a "nanobrick" morphology that greatly increases the tortuous pathway for diffusing molecules. The LBL coating depicted here possesses 5 polyelectrolyte/nanoclay bilayers (BLs).

Scheme 1. Chemical structures of the two polyelectrolytes employed as adhesives in this study: polyethyleneimine (PEI) and poly(ethylene terephthalate) ionomer (PETi).

complex with the platelets and thereby stabilize the coating. Such coatings exhibit remarkable barrier properties, with reductions in O_2 permeability of over 3 orders of magnitude reported [26] for LBL coatings composed of 24 bilayers (where *bilayer*, BL, refers to one polyelectrolyte layer and an adjacent nanoclay layer). Most commercial polymers employed in packaging are inherently hydrophobic, in which case their surfaces are often modified by different treatment methods (e.g., O_2 plasma, coronal discharge, ultraviolet ozone, and chemical reactions) to introduce polar moieties and improve surface wettability [20,27,28]. Although the barrier properties of LBL coatings have been the subject of numerous studies (primarily focusing on O_2 permeation), the present work aims to extend the current understanding of such coatings by investigating the effect of temperature on both O_2 and CO_2 permeation. In addition, the barrier efficacy of a polyanion that can complex with the positive charges that accumulate on the edges of MMT platelets [29–31] is examined and quantitatively compared with that of PEI.

2. Experimental

2.1. Materials

A polystyrene (PS) homopolymer with a number-average molecular weight ($\overline{M}_n$) of 100 kDa and a polydispersity index (PDI) of 1.01, according to size-exclusion chromatography (SEC), was synthesized by living anionic polymerization and was utilized as the substrate for LBL coatings in transmission electron microscopy (TEM) images due to ease of sectioning at ambient temperature. A commercial random poly(styrene-*co*-butadiene) (SB) copolymer ($\overline{M}_n$=95.4 kDa and PDI=1.85 from SEC) containing 4.0 wt% B according to the supplier was purchased from Sigma-Aldrich (St. Louis, MO) and used as the substrate for LBL coatings in permeation tests due to its rubber-improved fracture resistance. A branched PEI ($\overline{M}_n$=60 kDa and PDI=12.5, according to the manufacturer) with good thermal stability [32,33] was obtained from Scientific Polymer Products (Ontario, NY), whereas an AQ55S poly(ethylene terephthalate) ionomer (PETi) ($\overline{M}_n$≈10 kDa [34]) was generously donated by Eastman Chemical Company (Kingsport, TN). The chemical structures of these two polyelectrolytes are depicted in Scheme 1. Purified Na$^+$MMT nanoclay with a cation exchange capacity [29] of 0.92 meq/g was procured from Southern Clay Products (Gonzales, TX). Ultrahigh-purity (99.999%) O_2
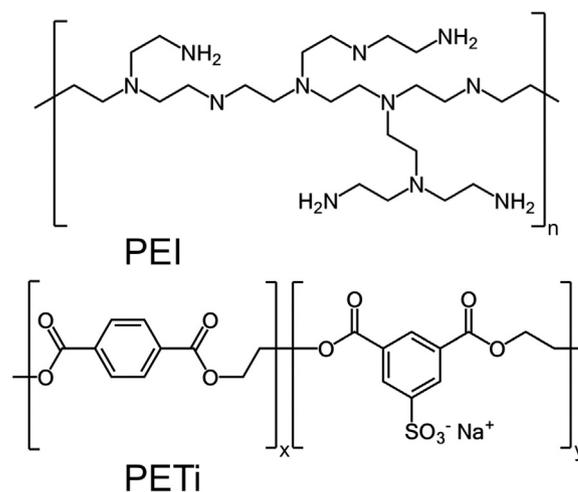
and high-purity (at least 99.9%) CO_2 were purchased from National Welders Supply Co. (Charlotte, NC) and Air Liquid America Specialty Gases (Plumsteadville, PA), respectively. The resistivity of deionized water (DIW), prepared with the Millipore Direct-Q 3 UV purification system and used primarily as the liquid medium for polyelectrolyte solutions and MMT suspensions, was 18.2 MΩ at 25 °C.

2.2. Methods

2.2.1. Specimen preparation

Polymer films typically measuring 100 µm thick were prepared on crystallization plates by solution casting from toluene at ambient temperature. Resultant films were annealed under vacuum for 24 h in the melt at 110 °C (above the PS glass transition temperature, T_g, of 100 °C) to ensure complete solvent removal. The films were then exposed to O_2 plasma generated in a low-pressure FEMTO plasma system (Diener Electronic GmbH, Ebhausen, Germany) operated at a power of 10 W/cm^2 and a gas flow rate of 20 sccm (standard cm^3/min) for 60 s to introduce polar organic moieties and thus enhance surface hydrophilicity and polyelectrolyte adhesion. Polyelectrolyte solutions were prepared by dissolving PEI at concentrations of 0.1, 0.5, 1.0 and 10 wt% in DIW by continuous stirring at ambient temperature. In the case of PETi, identical solutions were produced for comparison, but dissolution was conducted at 60 °C (above the PETi T_g of 52 °C). Four MMT suspensions at 0.1, 1.0, 3.0, and 5.0 wt% in DIW were ultra-sonicated for 20 min, followed by continuous stirring at ~600 rpm for 24 h, to achieve stable exfoliation and homogeneity. Each plasma-treated film was immersed in a predetermined polyelectrolyte solution for 5 min, rinsed with DIW to remove excess polymer and dried with filtered air. The polyelectrolyte-coated film was subsequently immersed in one of the MMT suspensions to deposit a layer of MMT platelets and produce the first BL. This sequence of events, conducted at ambient temperature and air-dried after each cycle, was repeated until a desired number of BLs accumulated on each specimen.

2.2.2. Specimen characterization

Electron-transparent sections for TEM analysis were generated by first embedding LBL-coated PS films in epoxy and then cross-sectioning the resulting composites in a Leica Ultracut 7 ultramicrotome at ambient temperature. Digital TEM images of sections measuring ~120 nm thick and floated onto carbon-coated copper grids were acquired on a JEOL 2000-FX microscope operated at an accelerating voltage of 200 kV. Wide-angle X-ray diffractometry (XRD) was performed at ambient temperature on an Inel XRG 3000 diffractometer (Artenay, France) with CuKα radiation possessing a wavelength (λ) of