

Short communication

Oxygen barrier of multilayer thin films comprised of polysaccharides and clay



Galina Laufer, Christopher Kirkland, Amanda A. Cain, Jaime C. Grunlan*

Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, United States

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ABSTRACT

Multilayered thin films of chitosan (CH), carrageenan (CR) and montmorillonite (MMT) clay, deposited using the layer-by-layer technique, were studied in an effort to produce fully renewable polysaccharide-based thin films with low oxygen permeability. Ten 'trilayers' of CH/MMT/CR (<40 nm thick) on PET film reduced its oxygen permeability ($1.76 \times 10^{-15} \text{ cm}^3 \text{ cm/cm}^2 \text{ s Pa}$) by an order of magnitude under dry conditions. By adding an additional layer of CH to the trilayer sequence, a 'quadlayer' film of CH/CR/CH/MMT (<60 nm thick) was created, which was able to reduce oxygen permeability of PET by two orders of magnitude under the same conditions. This high oxygen barrier is believed to be due to the unique nanostructure of these films, often referred to as a "nanobrick wall" structure, as well as a strong association amongst the oppositely charged polysaccharides. Combining fully renewable and food contact approved ingredients with high gas barrier and optical transparency makes this technology promising as a foil replacement for food packaging.

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1. Introduction

Recently, much attention has been devoted to using bio-based materials as an alternative to man-made polymers for food packaging applications (Bastioli, 2001; Davis & Song, 2006; Eichhorn & Gandini, 2010). Amongst these materials are chitosan and carrageenan, both of which are nontoxic, biodegradable and exhibit antimicrobial properties (Choi et al., 2005; Rabea, Badawy, Stevens, Smaghe, & Steurbaut, 2003). These polysaccharides already have wide application in the food industry (Bixler, 1996; Hambleton, Fabra, Debeaufort, Dury-Brun, & Voilley, 2009) (Lee, Lim, Chong, & Shim, 2009) because they are Generally Recognized as Safe by the U.S. Food and Drug Administration (FDA) (CFR 172.620; GRN No. 170). Carrageenan (CR), which is an anionic sulfated polysaccharide extracted from red seaweeds (McHugh, 1987), and cationic chitosan (CH) extracted from the shells of crustaceans (El-Tahlawy & Hudson, 2006), have already been shown to have oxygen barrier properties (Gallstedt & Hedenqvist, 2002; Hambleton, Debeaufort, Beney, Karbowiak, & Voilley, 2008), but this barrier can be further improved by incorporating montmorillonite (MMT) clay. MMT has been widely studied as an additive to reduce the gas permeability of various polymers (Priolo, Gamboa, & Grunlan, 2010; Triantafyllidis, LeBaron, Park, & Pinnavaia, 2006).

In this study, coatings of renewable food contact approved materials (i.e., chitosan, carrageenan and clay) on PET with varying clay spacing, achieved through layer-by-layer (LbL) deposition, are evaluated for their oxygen permeability at 23 °C and 0% RH. Thickness as well as oxygen barrier of these thin film assemblies can be tailored by altering spacing between clay layers. A film consisting of ten trilayers of CH/MMT/CR reduced oxygen permeability of PET film by an order of magnitude, at a thickness of only 35 nm. Alternately, thicker films (~55 nm) with a quadlayer structure (i.e., CH/CR/CH/MMT) showed greater barrier by reducing oxygen permeability of PET by two orders of magnitude. This relatively simple technology, using renewable ingredients, may be of use for a variety of food packaging applications.

2. Experimental

2.1. Materials

Chitosan (Aldrich, Milwaukee, WI) (MW 50–190 kDa, 75–85% deacetylated) was dissolved in deionized water (18.2 MΩ) to create a 0.2 wt% solution. The pH of this solution was increased to 6 with 1 M sodium hydroxide (NaOH). λ-Carrageenan (Aldrich) was used as a 0.1 wt% solution in deionized water. The pH of this solution was adjusted to 3 with HCl. Sodium montmorillonite clay (tradename Cloisite® Na⁺, Southern Clay Products, Inc., Gonzales, TX) suspensions were prepared at 1.0 wt% in deionized water. Single-side-polished (100) silicon wafers (University Wafer, South Boston, MA) were used as the substrate for film thickness

* Corresponding author. Tel.: +1 979 845 3027; fax: +1 979 862 3989.
 E-mail address: jgrunlan@tamu.edu (J.C. Grunlan).

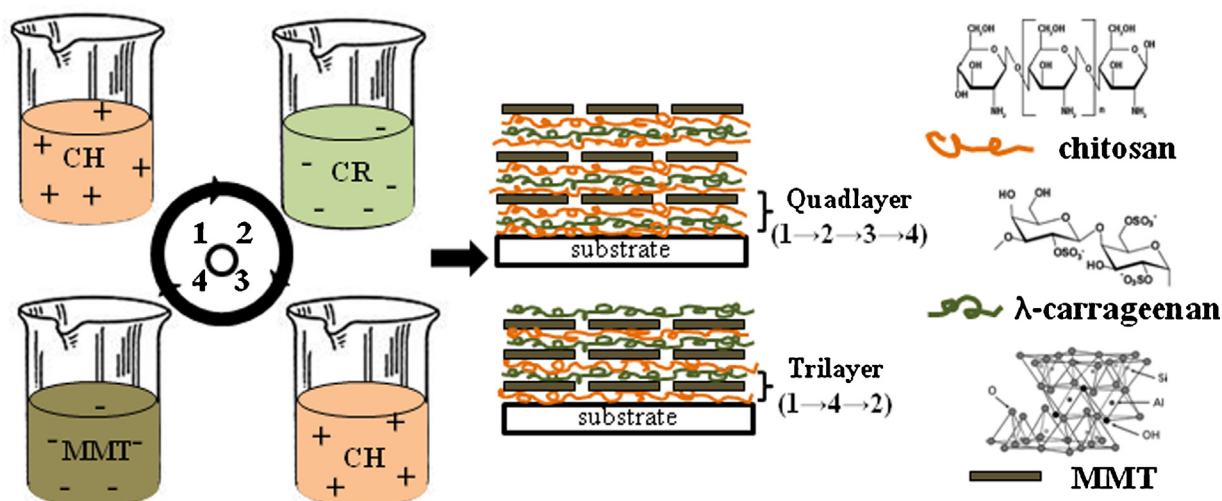


Fig. 1. Schematic of layer-by-layer assembly of renewable materials resulting in thin films with different clay spacing.

characterization and 179 μm thick poly(ethylene terephthalate) film (trade name ST505, produced by Dupont-Teijin), purchased from Tekra (New Berlin, WI), was used for oxygen barrier testing.

2.2. Film preparation

Prior to deposition, plastic substrates were corona treated with a BD-20C Corona Treater (Electro-Technic Products, Inc., Chicago) to create a negative surface charge. All films were deposited on a given substrate using the procedure shown schematically in Fig. 1. Substrates were alternately dipped into chitosan (CH), λ -carrageenan (CR) and montmorillonite (MMT). One cycle of CH/MMT/CR is referred as a trilayer (TL) and one cycle of CH/CR/CH/MMT is referred to as a quadlayer (QL). Initial dips for first two layers were 5 min each and subsequent dips were 1 min. Each dip was followed by rinsing with deionized water and drying with air.

2.3. Characterization

Film thickness was measured with an alpha-SE Ellipsometer (J. A. Woollam Co., Inc., Lincoln, NE). The weight per deposited layer was measured with a Maxtek Research Quartz Crystal Microbalance (RQCM) (Infinicon, East Syracuse, NY), with a frequency range of 3.8–6 MHz, in conjunction with 5 MHz quartz crystals. Clay concentration was measured by a Q50 Thermogravimetric Analyzer (TA Instruments, New Castle, DE) by heating 5–10 mg samples up to 1000 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Cross sections of chitosan-based assemblies were imaged with a JEOL 1200 EX TEM (JEOL Ltd., Tokyo, Japan), operated at 110 kV. Samples were prepared for imaging by embedding a piece of PET supporting the LbL film in epoxy and sectioning it with a microtome equipped with a diamond knife. Film absorbance was monitored at wavelengths between 190 and 900 nm using a USB2000 UV–vis Spectrometer (Ocean Optics, Dunedin, FL). Oxygen transmission rates were measured by MOCON (Minneapolis, MN) in accordance with ASTM D-3985, using an Oxtran 2/21 ML instrument at 23 $^{\circ}\text{C}$ and 0% RH.

3. Results and discussion

3.1. Film growth and microstructure

Fig. 2 shows the growth of these polysaccharide-based assemblies as a function of the number of cycles (trilayers or quadlayers) deposited. The CH–CR–CH–MMT system exhibits an increased

slope around the 4th QL, after which the average thickness increases from 3.5 nm to 5.8 nm for each QL. Interdiffusion of carrageenan could be the origin of this larger growth rate. The exponential growth observed for this system has been observed for a variety of other weak polyelectrolyte systems and its mechanism has been studied in great detail (Picart et al., 2002; Richert et al., 2004). It is unlikely that chitosan would be able to diffuse in and out of the film due to its rigidity (Laufer, Priolo, Kirkland, & Grunlan, 2013; Morris, Castile, Smith, Adams, & Harding, 2009), but CR is more flexible, having been shown to form soft films with weakly charged molecules like poly(allylamine hydrochloride) (Schoeler et al., 2006). CH is weakly charged at pH 6 (pK_a 6–6.5) due to deprotonation of its amine groups (Kurita, 2001). At pH 3, only some of the sulfate groups on the CR molecule are protonated ($\text{pK}_a \sim 2$), so CH and CR form weakly bonded multilayers (Gu, Decker, & McClements, 2005). Absence of strong bonds between CH and CR enables greater diffusion of CR molecules into the growing film.

No comparable slope change is observed in the trilayer system, consisting of CH/MMT/CR, which grows linearly as a function of cycles deposited. Although CR and MMT are both negatively charged, the successful film build up is possible because hydroxyl groups on carrageenan can form hydrogen bonds with the hydroxyl groups and oxygen on MMT. These relatively strong associations reduce the mobility of CR, making it unable to diffuse in and out of the film, resulting in linear growth. This trend was confirmed with quartz crystal microbalance (QCM) measurements. It has been reported that increasing the hydrophilicity of the surface during growth can cause greater weight to be deposited (Martins, Mano, & Alves, 2010). This has been observed for the systems studied here, where the highest weight deposited corresponds to a carrageenan layer. Water entrapment due to the hydrophilic character of CR is believed to be a key contributing factor (Pinheiro et al., 2012). Chitosan is relatively hydrophobic molecule and in this study it is used close to its solubility limit (Qin, Li, Xiao, Zhu, & Du, 2006; Zheng et al., 2009), which reduces water uptake in the adsorbed layer and results in a smaller measured mass (Indest et al., 2008). It is assumed that the mass corresponding to the adsorption of CR includes entrapped water, preventing film composition from being determined by QCM measurements.

In an effort to overcome the challenges associated with QCM, clay concentration was measured using thermogravimetric analysis. 60 TL and 60 QL films that were heated to 1000 $^{\circ}\text{C}$ to burn off all of the polymeric components. Quadlayer and trilayer films were determined to have 33 wt% and 47 wt% clay, respectively. It

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