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# Enhanced water vapor barrier properties for biopolymer films by polyelectrolyte multilayer and atomic layer deposited $Al_2O_3$ double-coating

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ABSTRACT

Commercial polylactide (PLA) films are coated with a thin (20 nm) non-toxic polyelectrolyte multilayer (PEM) film made from sodium alginate and chitosan and additionally with a 25-nm thick atomic layer deposited (ALD) $Al_2O_3$ layer. The double-coating of PEM + $Al_2O_3$ is found to significantly enhance the water vapor barrier properties of the PLA film. The improvement is essentially larger compared with the case the PLA film being just coated with an ALD-grown $Al_2O_3$ layer. The enhanced water vapor barrier characteristics of the PEM + $Al_2O_3$ double-coated PLA films are attributed to the increased hydrophobicity of the surface of these films.



## 1. Introduction

Growing environmental concerns related to the use of synthetic polymers in packaging industry have led to the need for new bio-based materials [1]. The bio-based packaging materials currently in the market are mainly based on starch or polylactide (PLA). These materials have many advantages, such as sustainability, recyclability and biodegradability [2]. However, the sensitivity of biopolymers towards moisture has restricted their use. To overcome the problem various surface treatment approaches have been considered to enhance the water vapor barrier properties of biopolymers.

A simple and cost-effective way to functionalize surfaces is to coat them with a polyelectrolyte multilayer (PEM) film [3]. Ultra-thin PEM films can be prepared by a layer-by-layer (LbL) technique through alternating adsorption of cationic and anionic polyelectrolyte solutions. A charged substrate of any size or shape is immersed into a polyelectrolyte solution with a net charge opposite to the surface charge. The polymer is spontaneously adsorbed onto the substrate due to the electrostatic interactions [4,5], resulting in charge reversal at the surface [6,7]. Rinsing removes the unbound polymer from the surface. The LbL deposition technique is well suited for the construction of precise nanolevel architectures and there are several potential applications ranging from biomaterials [8] and drug delivery [9] to membranes [10].

Here we investigate the capability of PEM films together with a thin inorganic layer applied on top of it to improve water vapor barrier properties of PLA films. Our interest was to see how the PEM film as an intermediate layer would affect the surface properties of PLA and thereby the water vapor barrier properties of it after the surface is additionally coated with an $Al_2O_3$ layer grown by the atomic layer deposition (ALD) technique. The ALD technique is a self-limited surface controlled gas-phase deposition process perfectly suited to produce inorganic high-performance (i.e., homogeneous, pinhole-free and conformal) gas and vapor barrier coatings on polymers. Thin (5–25 nm) ALD-grown $Al_2O_3$ coatings have already been shown to be effective barrier layers towards gases and vapors [11–17]. The effect of surface nanostructure on the wettability properties has been demonstrated e.g., with ALD-grown ZnO coatings on cicada wings [18]. As a result of the self-limiting growth mechanism, the ALD coating follows closely the topography of the substrate, even on nanostructured surfaces [19–22].

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The nature-based polyelectrolytes sodium alginate (ALG) and chitosan (CHI) were selected for the LbL deposition of the PEM film. Chitosan is a suitable counter polyelectrolyte for moisture-sensitive ALG due to its good film-forming properties [2] and natural antibacterial and fungicidal properties make CHI an attractive polyelectrolyte for food and pharmaceutical packaging applications [23]. The fabrication of PEM films does not require any expensive equipment. The improvement in the water vapor properties of the PLA film by the intermediate PEM film could limit the amount of $Al_2O_3$ needed, thus improving the cost-efficiency of the fabrication process. Note that for the possible future utilization of thin $Al_2O_3$ coatings as a part of the fabrication line of bio-based packaging materials, the ALD is considered to be the most expensive process step.

## 2. Materials and methods

### 2.1. Fabrication of PEM films for their preliminary characterization

Polyelectrolyte multilayer films from ALG and CHI (extracted from chitin according to [24]) were first deposited on silicon wafers for preliminary tests for the film thickness and cytotoxicity. Exactly the same LbL method as used for the PLA substrates (see Section 2.2) was employed here. The LbL deposition process is also well described in literature [3,25]. The solutions of CHI and ALG were vacuum filtered in order to remove impurities. Prior to the LbL depositions the silicon (1 0 0) substrates employed were purified and silanizated. The substrates were dipped into acetone (99.5 vol.%) for 15 min, rinsed with distilled water, followed by dipping into warm (60 °C) solution of 5:1:1 $H_2O$:$NH_4OH$ (25 vol.%):$H_2O_2$ (30 vol.%) for 60 min. Then the substrates were rinsed again with distilled water and dipped into a warm (60 °C) solution of 3:1 $H_2SO_4$ (95–97 vol.%): $H_2O_2$ (30 vol.%) for 60 min. Finally, the substrates were rinsed with distilled water and dried with pressurized air. Prior to the silanization, the silicon wafers were kept in an oven at 110 °C for overnight. The silanization was performed by dipping the substrates into (3-aminopropyl)triethoxysilane in dry toluene solution (1 vol.%) at 60 °C for 4 min. After the silanization, the substrates were dipped into toluene and dried with pressurized air.

### 2.2. PEM and $Al_2O_3$ depositions on PLA biopolymer film

Commercial PLA film with a thickness of 20 μm was selected as a representative biopolymer substrate for the depositions. The substrate was first coated with a PEM film using the LbL process and subsequently with an $Al_2O_3$ layer. For the LbL fabrication of PEM films, four solutions were made: anionic ALG and cationic CHI solutions plus rinsing buffer and rinsing water solutions with the following concentrations: c(ALG) = c(CHI) = 1 mg/ml; c(NaCl) = 0.15 M, and c(AcOH) = 1 mM. In order to improve the solubility of CHI, HCl (c(HCl) = 10 mM) was added. The pH of the solutions was adjusted to 4.5 using NaOH. The PLA substrates were sequentially dipped into ALG and CHI for 15 min. Between the dippings the substrates were dipped into rinsing solutions, three times into buffer solution for 60 s followed by dipping into distilled water for 60 s and drying with nitrogen. Eleven single layers were deposited on three parallel samples. The deposition began and ended with a layer of CHI leaving CHI as the outermost layer facing the $Al_2O_3$ layer.

The $Al_2O_3$ depositions were carried out in a commercial SUNALE™ R-series ALD reactor at 100 °C targeting at a $Al_2O_3$ layer thickness of 25 nm. Fig. 1 presents the targeted three-layer structure. The ALD precursors for the $Al_2O_3$ depositions were trimethylaluminum (TMA, SAFC Hitech, electronic grade purity) and water. High purity $N_2$ (99.9999%) was used as a carrier and purge gas. One ALD cycle consisted of a TMA precursor pulse and a subsequent $N_2$ purge followed by a water precursor pulse and another $N_2$ purge. The precursor pulses lasted 0.1 s and the purges 5 s. The resultant film thicknesses on the polymer films could not be directly measured. Instead, the coating thicknesses were produced according to the reactor process parameters and compared to the thickness of a similarly grown $Al_2O_3$ layer on a silicon wafer analysed with a Nanospec AFT4150 reflectometer. The film growth rate was estimated to be *ca* 1.1 Å/cycle. Due to the different surface chemistries the actual growth rate on the PLA substrate may however somewhat deviate from that determined for the $Al_2O_3$ coating on silicon wafer [26,27].

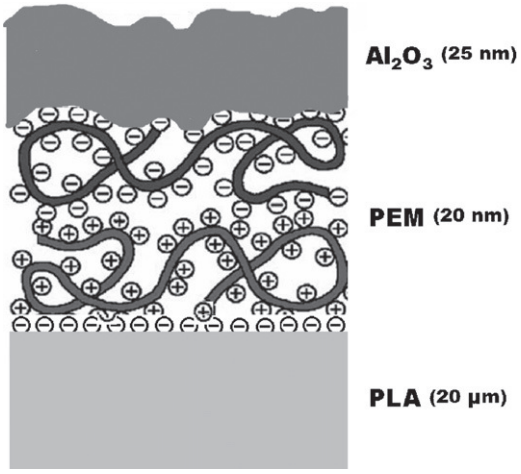


**Fig. 1.** Schematic illustration of the targeted multilayer structure of PEM- and $Al_2O_3$-coated PLA film.
Figure modified from that of G. Decher [3].

### 2.3. Characterizations

Molecular weights of the polyelectrolytes affect the formation of the film and its surface properties. Therefore the molecular weights of ALG and CHI were determined. Solutions of ALG and CHI with concentrations from 0 to $6 \times 10^{-4}$ g/ml were fabricated for the density and viscosity measurements. Molecular weights were determined by measuring densities with an Anton Paar DMA 45 digital density meter at 25 °C and viscosities with an Anton Paar AMVn automated microviscometer.

The Mark–Houwink equation (1) gives the relation between intrinsic viscosity $[\eta]_{in}$ and molecular weight $M_v$.

$$[\eta]_{in} = KM_v^a \quad (1)$$

From this equation the molecular weight of a polyelectrolyte can be determined using the intrinsic viscosity and the parameters, $a$ and $K$, from literature [28,29]. The thickness and the root-mean-square (rms) roughness value of the PEM film on silicon wafer was determined by a scanning spectroscopic ellipsometer (Nanofilm EP3).

The cytotoxicity of the PEM film from ALG and CHI was investigated. Cytotoxicity measures the toxicity of a material to living cells. The disinfected PEM films deposited on silicon wafer were kept in a Medium solution (DMEM, Dulbecco's modified Eagle's medium, Sigma) for 2 h at room temperature in humid conditions. The test cells were commercial CRL-2592 cells from ATCC. In the test the value of the lactate dehydrogenase (LDH) was determined and used to evaluate the toxicity. Two control samples were used: highly toxic polyvinyl chloride stabilized with organic tin compound as a

**Table 1**
Molecular weights of the polyelectrolytes ALG and CHI, together with the salts and their concentrations and the Mark–Howink parameters ($K$ and $a$) used in calculations.

| Species | Salt | $C$ (Salt) (M) | $K$ (ml/g) | $A$ | $[\eta]_{in}$ (ml/g) | $M_v$ (g/mol) |
|---|---|---|---|---|---|---|
| ALG | NaCl | 0.1 | 0.0073 | 0.92 | 760 | 280 000 |
| CHI | NaOAc/AcOH | 0.2/0.3 | 0.082 | 0.76 | 770 | 170 000 |

positive and non-toxic glass as a negative control. The cells were placed in direct contact with the samples. After 24 h the amount of LDH was measured by UV-Vis spectrophotometer and the cytotoxicity ($D$%) was determined [30]. In the case of the $D$% value being 15% or higher, the sample is considered to be toxic to living cells.

The water vapor transmission rate (WVTR) was measured from three parallel samples according to the modified gravimetric methods, ISO 2528:1995 and SCAN P 22:68, and was expressed as g/m$^2$/day. The test conditions were 23 °C and 75% relative humidity. Additionally, we investigated the wettability properties of the sample surfaces through contact angle (CA) measurements. The CA measurements were performed with KSV CAM 200 Optical Contact Angle Meter in a controlled atmosphere (relative humidity 50%, temperature 23 °C). The contact angle values of three parallel samples were calculated at the time of 1 s from the moment the water drop contacts the surface. The samples were also investigated by scanning electron microscopy (SEM; JEOL JSM-7500FA). For SEM, the samples were sputter-coated with a thin layer of platinum to promote conductivity.

## 3. Results and discussion

### 3.1. Properties of PEM films

The molecular weight values determined for the two polyelectrolytes, CHI and ALG, are presented in Table 1 together with the necessary parameters used to calculate these values. The values obtained for the molecular weights are consistent with those reported in literature [28,29].

Our aim was to prepare ultra-thin and PEM films from ALG and CHI. This was successfully realized and the average thickness of the films was measured (by scanning spectroscopic ellipsometry) to be 20 nm. The rms roughness in micrometer-scale of the PEM films on top of silicon wafer was determined to be 1.6 nm determined from the 300 μm × 300 μm image. The cytotoxicity tests revealed that the $D$% value was 3.53% thus verifying that the films were non-toxic to living cells and accordingly suitable to be used in food and pharmaceutical packaging applications.

### 3.2. Properties of PEM- and $Al_2O_3$-coated PLA films

The water vapor barrier and wettability properties of the PEM- and $Al_2O_3$-coated PLA films were evaluated by measuring the water vapor transmission rates and the contact angle values for a plain PLA film and for PLA films with various coatings. The results are summarized in Table 2. From Table 2 the positive effect of the PEM + $Al_2O_3$ double-coating on the water vapor barrier properties of PLA is clearly seen.

**Table 2**
Water vapor transmission rate (WVTR) and contact angle (CA) values for the plain and variously coated PLA samples. The given numbers are average values for three parallel samples.

| Sample | WVTR (g/m$^2$/day) | CA (°) |
|---|---|---|
| PLA | 53 ± 4 | 73 ± 2 |
| PLA + PEM | 106 ± 7 | 76 ± 4 |
| PLA + 25 nm $Al_2O_3$ | 33 ± 6 | 48 ± 1 |
| PLA + PEM + 25 nm $Al_2O_3$ | 25 ± 9 | 98 ± 4 |

The PEM-film coating alone did not improve the water vapor barrier properties of the PLA film, rather the WVTR of PLA was increased from 53 to 106 g/m$^2$/day after the PEM-film coating. This is apparently due to the dipping process in the LbL method exposing the hygroscopic PLA polymer chains to swelling. The ALD-grown $Al_2O_3$ layer alone enhanced the water vapor barrier properties of the PLA film considerably, as expected from our previous studies [11]. Here the WVTR value was found to decrease from 53 to 33 g/m$^2$/day. Most importantly, the PEM + $Al_2O_3$ double-coating improved the water vapor barrier properties even more by decreasing the WVTR value to 25 g/m$^2$/day.

The water vapor barrier level achieved here with the double-coating is close to the level required (0.1–10 g/m$^2$/day) in commercial packaging applications for dry food and pharmaceutics. The present results are significant due to the fact that the LbL deposition is a very cheap and easy-to-use method. It should also be emphasized that the ALD-grown $Al_2O_3$ layer is so thin that it should not affect the biodegradability of the material. In addition, the PLA film investigated here was relatively thin (20 μm) when considering typical packaging materials.

From Table 2, the water vapor transmission rates seem to correlate with the wettability properties of the ALD-$Al_2O_3$-coated samples such that the larger the CA is, the lower is the WVTR value. Polar $H_2O$ molecules are apparently less readily adsorbed on the less polar surface. The contact angle value of the plain PLA film was 73°. The PEM coating alone did not change the contact angle value considerably. However, when the PEM-coated PLA film was further coated with an $Al_2O_3$ layer, the contact angle value increased to 98° thus making the surface more hydrophobic. On the contrary, when the PLA film was coated only with the $Al_2O_3$ layer, the contact angle value was found to decrease to 48° making the surface rather more hydrophilic. This is rather what was expected due to the intrinsically hydrophilic nature of $Al_2O_3$ surfaces [31].

From the discussions above (Table 2) the PEM intermediate layer apparently influences the hydrophobicity of the $Al_2O_3$ surface. The very reason for that remains to be clarified more deeply in future

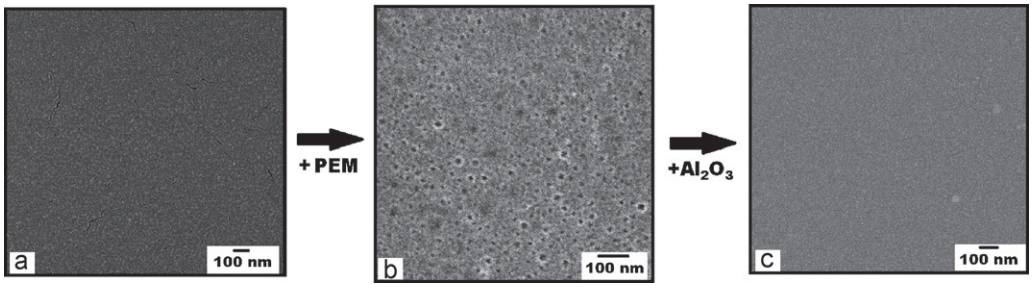


**Fig. 2.** SEM images for the plain and variously coated PLA films. (*a*) The plain PLA film appears to be smooth with small patterns due to the sputtered Pt. (*b*) The PEM-film-coated PLA film seems to have nanopores throughout the film. (*c*) After further coating with a 25-nm thick $Al_2O_3$ layer the surface seems to be conformally coated with the $Al_2O_3$ layer.

studies. However, parallel behavior (i.e., a CA value of 128°) was recently observed for a thermally grown $Al_2O_3$ coating with a relatively rough surface [32]. It is known that some special topologies of surface structure could produce even superhydrophobic states on intrinsically hydrophilic surfaces [33]. The LbL dipping process may alter the surface of the PLA film and increase its roughness.

In Fig. 2 we show SEM images taken from the plain and variously coated PLA films. It is seen that the PLA film is a very smooth substrate, presumably due to the commercial fabrication method of the film. Small surface patterns can be observed due to the sputtered Pt. Once the PLA film is coated with a PEM film, a surface structure with small pores (10–30 nm in diameter) appears on the surface of the whole film. After the further deposition of the 25-nm thick $Al_2O_3$ layer the nanostructured surface seems to be conformally coated with $Al_2O_3$, such that the smallest pores are filled but the surface still presents some surface structure. In order to gain deeper understanding of the reasons for the increased hydrophobicity efforts should be made to investigate the surface structures and chemistries in a much more detailed way.

## 4. Conclusions

Ultra-thin and non-toxic polyelectrolyte multilayer (PEM) films from sodium alginate and chitosan were successfully deposited onto commercial polylactide (PLA) biopolymer film, and further coated with a 25-nm thick atomic layer deposited (ALD) $Al_2O_3$ layer. The water vapor barrier properties of the PLA film were considerably improved after employing the PEM + $Al_2O_3$ double-coating. Most importantly, the properties were improved more than by applying just the $Al_2O_3$ coating. This was tentatively attributed to changes in surface morphology created by the PEM layer. The use of a thin PEM film as an intermediate on the PLA film prior to the $Al_2O_3$ coating could extend the use of biopolymers in environmentally friendly food and pharmaceutical packaging applications.

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