

PUBLICATION I

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Comparison of some coating techniques to fabricate barrier layers on packaging materials

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ABSTRACT

Atomic layer deposition (ALD), electron beam evaporation, magnetron sputtering and a sol-gel method were used to deposit thin aluminum oxide coatings onto two different fiber-based packaging materials of commercial board grades coated with synthetic and biodegradable polymers. Significant decreases in both the water vapor and oxygen permeation rates were observed. With each technique the barrier performance was improved. However, among the techniques tested ALD was found to be most suitable. Our results moreover revealed that biodegradable polylactic acid-coated paperboard with a 25-nm thick layer of aluminum oxide grown by ALD on top of it showed promising barrier characteristics against water vapor and oxygen.

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1. Introduction

Fiber-based packaging materials have many advantages over their plastic competitors, such as sustainability, recyclability and stiffness/weight ratio [1]. However, poor barrier properties and sensitivity towards moisture are the main challenges for their extended use. In order to improve the barrier properties packaging materials are often coated with polymers or laminated with other materials such as aluminum foils and plastic films. Most of the studies have concerned polyethylene (PE), accompanied mainly by ethyl vinyl alcohol and poly(ethylene terephthalate) [1]. In recent years environmental aspects have become important and considerable efforts have been made to replace fossil-based raw materials by environmentally friendly, biodegradable or recyclable materials from natural sources.

The general permeation process through non-porous materials includes collision with the polymer surface and sorption on the high permeant concentration side, diffusion through the material and finally desorption of the permeant on the low concentration side. Mass transfer properties of polymer films define the permeation process. Diffusion, solubility and permeability are among the parameters used to describe the mass transfer for a specific material/permeant combination [2,3]. Permeability is an important parameter, which measures the overall transfer rate through a polymer film [2].

When considering polymer-coated paperboards, the water vapor transmission rate (WVTR) is affected by e.g. the coating weight of the polymer as well as the temperature and humidity of surroundings [4]. The common synthetic moisture barrier polymers include low- and high-density polyethylenes, polypropylene and polyethylene terephthalate [5]. Other polymers with moisture barrier properties include cyclo-olefin copolymers, liquid-crystal polymers and nanocomposites [6,7]. Hygroscopic materials, such as many biopolymers, typically lose their barrier properties at high relative humidity. This is due to absorption of water and swelling of the polymer which results in a more porous or open structure [8]. Therefore, efforts have been made to improve the water vapor and oxygen barrier properties by coating such materials by e.g. thin glass-like SiO_x coatings [6,9].

Atomic layer deposition (ALD) is a surface controlled layer-by-layer process based on self-terminating gas-solid reactions and is uniquely suited to produce high-performance gas diffusion barrier coatings on porous materials as it allows preparation of dense and pin-hole-free inorganic films that are uniform in thickness even deep inside pores, trenches and cavities of various dimensions. In our previous work [10] we demonstrated that a thin layer of Al₂O₃ deposited by the ALD technique is an efficient way to improve the barrier properties of sensitive packaging materials such as various uncoated papers, polymer-coated papers and boards and plain polymer films. The suitability of ALD to produce high-performance barriers has also been studied elsewhere [11–13]. Especially Al₂O₃ depositions have been used to produce gas diffusion barriers on polymers. One of the problems of coating barrier layers on packaging materials is poor flexibility. Liang et al. previously reported an

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alternative method of barrier membrane fabrication by ALD [14]. Membranes made from polymer/ceramic nanocomposite were fabricated by extruding ALD- Al_2O_3 coated micron-sized high-density polyethylene particles. According to Liang et al., the difficulty seems to be the interface between the polymer and the ALD- Al_2O_3 layer. Due to the different surface properties of these materials voids are formed during extrusion. Parallel results have been reported also elsewhere [15–20]. There is a need to upgrade the existing packaging materials, and thin inorganic coatings are an interesting way to create high-performance materials for food packages.

Despite of its obvious advantages, ALD is in its current form a time consuming and relatively expensive process. In this work the aim was to clarify whether the ALD technique could be replaced with other techniques and still produce as efficient barriers toward gases as with the ALD technique. For the comparative techniques, magnetron sputtering (MS), electron beam evaporation (EBE) and a sol-gel (SG) method were chosen, as they have been in general employed to produce coatings with relatively good or excellent barrier properties [6,21,22].

2. Experimental details

Commercial-grade paperboards (provided by Stora Enso Oyj) with synthetic low-density polyethylene (LDPE) and biopolymer polylactic acid (PLA) coatings on one side as summarized in Table 1 were used as test substrates. The substrates were ca. $10 \times 10 \text{ cm}^2$ in size. On these substrates Al_2O_3 coatings aiming at thicknesses of 25, 50 and 100 nm were deposited at temperatures below 100°C by means of the four comparative thin-film techniques tested, i.e. ALD, MS, EBE and SG. The processes employed are well established and accordingly the actual thicknesses of the Al_2O_3 layers are believed to deviate at most by few nanometers from the target values.

The ALD- Al_2O_3 depositions of 250, 500 and 1000 cycles were carried out in a Picosun SUNALE™ reactor at 100°C reaction temperature. Depositions were made on silicon wafers and paperboard samples. Trimethylaluminum (TMA, electronic grade purity, SAFC Hitech) and water were used as precursors. High purity nitrogen (99.9999% N_2) was used as carrier and purge gas. The precursors were evaporated at near room temperature and a deposition sequence was: 0.2 s TMA pulse, 4 s purge, 0.1 s water pulse, and 15 s purge. The operating pressure was 500–1000 Pa. The resultant film growth rates and actual film thicknesses on the polymer-coated boards could not be directly measured. Instead, we estimated the film thicknesses based on the growth rate determined to be 0.094 nm/cycle with a Nanospec AFT4150 reflectometer for films grown with the same TMA- H_2O ALD process on a silicon wafer Si(100). It should however be emphasized that because of the different polarities and functional groups of the PE and PLA surfaces the actual growth rates on our polymer-coated board substrates may somewhat deviate from that determined for the ALD- Al_2O_3 coating on flat silicon wafer [23,24]. Although the aim was to deposit only on the polymer-coated side, film growth also on the uncoated side could not be totally prevented.

The MS- Al_2O_3 films were deposited using a Sloan SL1800 magnetron sputtering deposition system. One single rectangular aluminum target was used. The sputtering gases were Ar and O^{2-} ,

the latter being the reactive gas for oxide film formation. Stoichiometry of the film was controlled using in-situ optical emission monitor feedback from the target emission lines [25]. Pulsed DC power was applied to the aluminum target at a frequency of 150 kHz and a pulse off time of 1000 ns. The target was operated in the controlled current mode, fixed at 3 A. The background pressure in the chamber was $0.2\text{--}2.6 \times 10^{-4}$ Pa and the sputtering pressure during the Al_2O_3 deposition was around 0.28 Pa. The thicknesses of the deposited films were measured from Si(100) reference samples by spectroscopic ellipsometry. The temperature of the substrate was monitored by means of temperature-sensitive tapes attached to the substrate surface to assure that it remained below 100°C during the depositions. For comparison, pure aluminum films with a thickness of 50 nm were also grown by the MS technique on both substrate materials. This was made because as a thicker film, metallic Al is considered to be a high-performance barrier.

The equipment used in the EBE- Al_2O_3 depositions was a UHV-class electron beam gun evaporator. The distance from the Al_2O_3 source was approximately 30 cm. Before the depositions the chamber was flushed with dry N_2 gas in order to improve the pumping efficiency. The chamber was pumped into pressure of $0.1\text{--}1 \times 10^{-5}$ Pa. After this the electron beam of 200–250 W was focused on the Al_2O_3 source with a voltage of 6.55 kV. The area of the electron beam was 3–6 mm^2 . The deposition rate was 0.3–0.5 nm/min.

For the SG- Al_2O_3 depositions the substrates were pretreated with plasma in order to clean the surface before the depositions. The SG solution was a mixture of water and alcohol and it was catalyzed with acid. Aluminum alkoxide was used as a precursor. The SG solution was sprayed on the substrate and hardened in an oven. The temperature of the oven was kept below 100°C . It should be noted that pure Al_2O_3 depositions are not possible with the SG technique but traces of organic molecules will be always present in the film due to the precursor solution. The thicknesses of the SG- Al_2O_3 layers deposited on Si(100) substrates were measured with the spectrophotometric modeling method described by Ylilammi and Ranta-aho [26]. The reflectance spectra for thickness modeling were recorded with a Hitachi U-2000 spectrophotometer in the 190–1100 nm wavelength range and modeling was performed with the Thinfilm program.

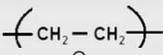
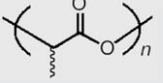
Images were taken of the uncoated substrates with an atomic force microscope (AFM; Park Systems XE-100) in order to clear their surface morphologies. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were carried out in order to determine the amount of aluminum in the ALD- Al_2O_3 deposited samples. Test pieces of the substrates before and after each ALD treatment were ignited and dissolved in an alkali metal melt. The results are expressed as mg/m^2 . Two to three parallel analyses from every sample were performed.

All the samples together with the uncoated substrate materials used were characterized for their oxygen transmission rate (OTR) expressed as $\text{cm}^3/\text{m}^2/10^5 \text{ Pa/day}$ and water vapor transmission rate (WVTR) expressed as $\text{g/m}^2/\text{day}$. The OTR measurements were carried out using humid gases with Mocon OXTRAN equipment such that the Al_2O_3 -deposited side of the sample faced the carrier gas stream. The measurements were performed at room temperature (23°C) and at 50–60% relative humidity. Two to three parallel samples were measured. The WVTR measurements were carried out for five parallel samples according to the modified gravimetric methods ISO 2528:1995 and SCAN P 22:68. The test conditions were 23°C and 75% relative humidity.

3. Results and discussion

Fig. 1 presents AFM images of the two uncoated substrate materials, B(PE) and B(PLA). The surface of B(PLA) appears to be smoother than that of B(PE). This might be due to its larger polymer-coating weight (35 g/m^2) in comparison to that for B(PE) (15 g/m^2),

Table 1
Commercial substrates used in the deposition tests.

Code	Description	Skeletal of the polymer
B(PE)	Low-density polyethylene (LDPE) coated (15 g/m^2) board	
B(PLA)	Polylactic acid (PLA) polymer-coated (35 g/m^2) board	

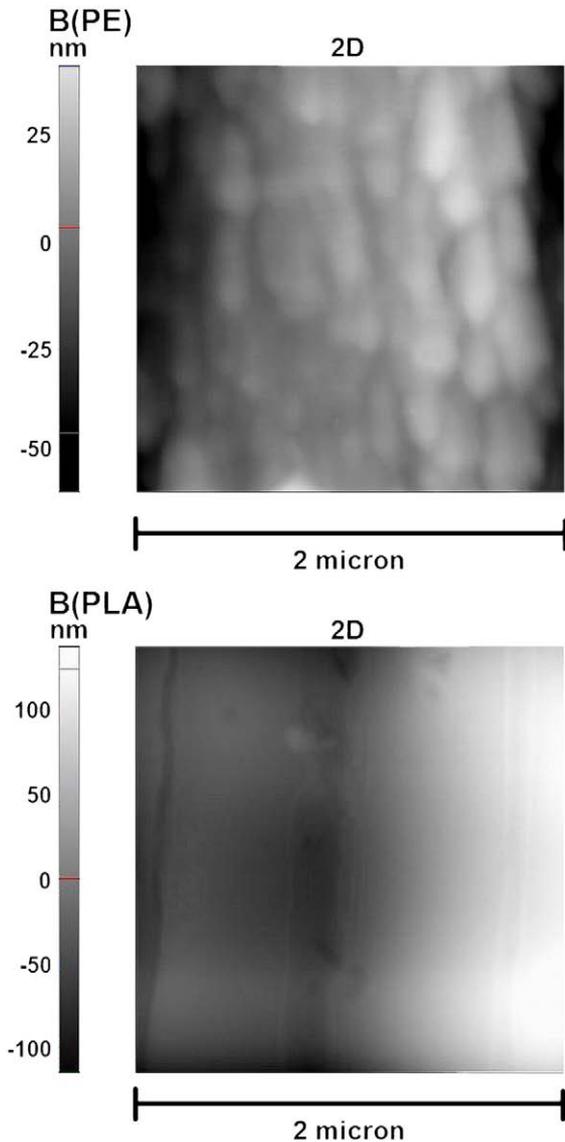


Fig. 1. AFM images of PE-coated paperboard (B(PE)) and PLA-coated paperboard (B(PLA)) substrate materials.

see Table 1. Another explanation could be the different chill roll surface patterns used in extrusion coating of the paperboard.

Due to their different surface roughness, the two substrate materials apparently accommodate different amounts of Al₂O₃ during parallel ALD treatments. In Table 2, ICP-AES results for the Al contents (expressed in mg/m²) in the various ALD-Al₂O₃ treated B(PE) and B(PLA) samples are summarized. The results are given as average ± standard deviation of two to three parallel analyses. It can be seen from Table 2 that the Al content increases with increasing number or ALD cycles or increasing Al₂O₃-film thickness. Compared to the smoother B(PLA) substrate, the B(PE) substrate has larger specific

Table 2
ICP-AES results for the Al content in ALD-Al₂O₃ coated B(PE) and B(PLA) samples. The results are given as average ± standard deviation of two to three parallel analyses.

	Al content (mg/m ²)	
	B(PE)	B(PLA)
25 nm ALD-Al ₂ O ₃	260 ± 3	96 ± 0.2
50 nm ALD-Al ₂ O ₃	650 ± 260	380 ± 150
100 nm ALD-Al ₂ O ₃	860 ± 200	495 ± 78

surface area and accordingly larger concentration of surface sites to accommodate larger amounts of TMA and water molecules upon the ALD depositions. The results show, however, that the standard deviations with the thicker (50 and 100 nm) films are greater than those with the thinner (25 nm) films. The porosity and the variances in porosity within pristine substrate materials may explain this. This may partly be also due to the different polarities of the polymer surfaces leading to different nucleation periods needed for the ALD-Al₂O₃ film growth as explained elsewhere [23,24].

Results from the oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) measurements are presented in Tables 3 and 4, respectively. Based on the results the positive effect of a thin Al₂O₃ layer on both the OTR and WVTR values is evident. The oxygen barrier performance of B(PLA) remains better than that of B(PE) independent of the thickness of the Al₂O₃ layer and the deposition technique employed. Tables 3 and 4 also reveal that the ALD technique is the best among the coating techniques investigated. Most impressively, when coating B(PLA) with a 25-nm thick Al₂O₃ layer by means of ALD, both the OTR (21 cm³/m²/10⁵ Pa/day) and WVTR (1.4 g/m²/day) values are excellent. In terms of the oxygen barrier property this sample is even better than the one coated with metallic aluminum by means of the MS technique (26 cm³/m²/10⁵ Pa/day).

The barrier performances of B(PE) and B(PLA) coated with Al₂O₃ by different techniques were found quite different. This could be due to the different ability of different techniques to form high-quality conformal films under the chosen deposition conditions. ALD is the only technique where the substrate is most perfectly and conformally coated from all sides. The probability of a pin-hole extending through the thin film or the whole material is smaller when the film is constructed of layer-by-layer deposited Al₂O₃ coating compared to a single deposition. In addition, the moisture being removed from the board during the deposition may affect the processes utilizing lower pressures, such as the MS technique.

The barrier properties of the pristine substrates were different making the reference level very different for these two substrates. Nevertheless, based on the results from OTR and WVTR measurements it seems to be so that when the substrate is rough a thicker Al₂O₃ layer is needed to block the diffusion of oxygen and water molecules. If the substrate is smooth a thinner Al₂O₃ barrier layer is enough; an excessively thick Al₂O₃ layer on top of a smooth substrate may be rather prone to cracking, which in turn impairs the barrier properties. It should also be emphasized that the two substrate materials used possess different surface chemistries. There are significantly fewer

Table 3

Oxygen transmission rates of uncoated, Al₂O₃-coated and Al-coated B(PE) and B(PLA) samples. The results are given as average ± standard deviation of two to three parallel measurements.

Deposition technique	OTR (cm ³ /m ² /10 ⁵ Pa/day)			
	ALD	MS	EBE	SG
B(PE) uncoated	7900 ± 1600	7900 ± 1600	7900 ± 1600	7900 ± 1600
B(PE) + 25 nm Al ₂ O ₃	6700 ± 2500	>10 000 ^a	3900 ± 1900	8300 ± 2400
B(PE) + 50 nm Al ₂ O ₃	2700 ± 400	>10 000 ^a	5200 ± 400	7400 ± 3600
B(PE) + 100 nm Al ₂ O ₃	2300 ± 100	>10 000; 645 ^b	3300 ± 600	8400 ± 2200
B(PE) + 50 nm Al	–	>10 000 ^a	–	–
B(PLA) uncoated	420 ± 10	420 ± 10	420 ± 10	420 ± 10
B(PLA) + 25 nm Al ₂ O ₃	20 ± 3	160 ± 120	150 ± 10	460 ± 10
B(PLA) + 50 nm Al ₂ O ₃	60 ± 5	85 ± 85	300 ± 140	400 ± 10
B(PLA) + 100 nm Al ₂ O ₃	200 ± 40	65 ± 0.5	210 ± 15	370 ± 10
B(PLA) + 50 nm Al	–	26 ± 1	–	–

^a The reliable detection limit with this OTR equipment is 10 000 cm³/m²/10⁵ Pa/day.

^b Great variation between parallel samples, average could not be reliably calculated.

Table 4

Water vapor transmission rates of uncoated, Al₂O₃-coated and Al-coated B(PE) and P(PLA) samples. The results are given as average ± standard deviation of five parallel measurements.

Deposition technique	WVTR (g/m ² /day)			
	ALD	MS	EBE	SG
B(PE) uncoated	7.0 ± 0.9	7.0 ± 0.9	7.0 ± 0.9	7.0 ± 0.9
B(PE) + 25 nm Al ₂ O ₃	6.9 ± 0.1	3.5 ± 1.0	5.7 ± 1.2	9.2 ± 3.3
B(PE) + 50 nm Al ₂ O ₃	2.0 ± 0.5	2.4 ± 0.9	3.9 ± 0.3	6.8 ± 0.5
B(PE) + 100 nm Al ₂ O ₃	2.0 ± 0.5	2.8 ± 1.3	3.7 ± 0.3	6.4 ± 0.6
B(PE) + 50 nm Al	–	2.0 ± 1.2	–	–
B(PLA) uncoated	64.9 ± 1.6	64.9 ± 1.6	64.9 ± 1.6	64.9 ± 1.6
B(PLA) + 25 nm Al ₂ O ₃	1.4 ± 0.2	11.0 ± 5.0	25.9 ± 2.7	62.5 ± 1.0
B(PLA) + 50 nm Al ₂ O ₃	1.8 ± 0.5	0.5 ± 0.1	21.8 ± 4.2	62.3 ± 1.9
B(PLA) + 100 nm Al ₂ O ₃	29.1 ± 5.1	1.9 ± 0.6	21.6 ± 7.1	62.0 ± 0.6
B(PLA) + 50 nm Al	–	1.3 ± 0.5	–	–

functional groups on the surface of B(PE) compared to the functional OH[−] groups on the surface of B(PLA). The lack of functional groups at surface may lead to poor bonding between the polymer surface and the Al₂O₃ layer. The lack of functional groups may also lead to cracking after the Al₂O₃ layer has been deposited.

The paperboard itself and even more significantly the polymer coating on top of it have an effect on the barrier performance of the final Al₂O₃-coated sample. Among the two polymers (at least in pure form), the melting point and the glass transition temperature are higher for PLA than for LDPE, making PLA more stable under the presently employed deposition conditions. At elevated deposition temperatures (around 100 °C) the polymer chains of LDPE start to move which may create pores and result in poor film growth. As a general observation from the OTR and WVTR values given in Tables 3 and 4, it is clear that with both the substrate materials the relation between the Al₂O₃-layer thickness and the gas barrier performance was not completely linear. The results for e.g. MS-Al₂O₃ treatments showed a very irregular behavior. This is at least partly due to the fact that the substrate is somewhat sensitive to the treatment conditions and thus the barrier performance varies accordingly. Although the ALD-Al₂O₃ layer deposited at 100 °C should be amorphous, the Al₂O₃ layer has also an effect on the cracking behavior as partial crystallization of the polymer coating on the substrate may cause interfacial tension between the Al₂O₃ layer and the polymer coating. This means that in practice a thicker inorganic film does not necessarily lead to improved barrier properties. This was in particular clear with the ALD-grown films, as even very thin films grown by the ALD technique are known to be highly conformal, dense and pin-hole free. Here, among the ALD-treated samples the best results were gained for samples with a 25-nm or 50-nm (but not 100-nm) thick ALD-Al₂O₃ coating. For the MS-grown films the film thickness had to be approximately doubled to achieve the same barrier level, see Tables 3 and 4. The growth circumstances were not optimized to these substrates during the depositions which may lead to better barrier results in the future.

When compared to the OTR and WVTR results in our previous studies [10] the results in this paper are better. This is due to several factors; the quality of the substrate materials may differ between different manufacturing lots. The tests indicate that the materials used in this study were better barriers as such. The other plausible explanation for the different barrier performance could be that in this study we used TMA with higher purity and 20 °C higher deposition temperatures. These could influence on the quality and conformality of the ALD-Al₂O₃ coating.

4. Conclusions

Thin (25–100 nm) layers of Al₂O₃ were grown at low temperatures on two types of polymer-coated paperboards by means of four

different thin film deposition techniques, i.e. atomic layer deposition (ALD), magnetron sputtering (MS), electron beam evaporation (EBE) and a sol-gel (SG) method. The aim of the work was to compare the different deposition techniques for their capability to produce high-quality gas barrier layers on top of commercial paperboard packaging materials. Despite the substrate material and the deposition technique employed, the gas barrier properties were significantly improved once the packaging material was coated with a thin layer of Al₂O₃. Among the four deposition techniques investigated, the best results were obtained with the ALD technique, followed by the MS technique. ALD technique was best among these techniques because the ALD-grown Al₂O₃ layers were most dense and the deposition conditions were most suitable for these sensitive materials in the ALD reactor. Films grown by ALD are typically highly conformal, dense and pin-hole free and therefore even nanometer-scale films are thick enough to work as efficient gas barriers. Paperboard coated with polylactic acid (PLA) polymer and a 25-nm thick ALD-grown Al₂O₃ layer was found as a highly promising barrier against oxygen and water vapor.

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