

PUBLICATION II

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Atomic layer deposited aluminum oxide barrier coatings for packaging materials

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ABSTRACT

Thin aluminum oxide coatings have been deposited at a low temperature of 80 °C on various uncoated papers, polymer-coated papers and boards and plain polymer films using the atomic layer deposition (ALD) technique. The work demonstrates that such ALD-grown Al₂O₃ coatings efficiently enhance the gas-diffusion barrier performance of the studied porous and non-porous materials towards oxygen, water vapor and aromas.

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1. Introduction

Various future distribution channels and the key role of packaging in ensuring the quality and safety of a wide variety of food items will increase the need for better packaging materials. Here the paper and board industry has to compete with the plastics industry for the market share. Fiber-based packages have advantages over their plastic competitors, such as sustainability, recyclability and stiffness/weight ratio. However, poor barrier properties and sensitivity towards moisture are some of the main challenges of the fiber-based materials. On the other hand, oil-based barrier coatings create problems for recycling. Development of biomaterials to replace the currently used oil-based ones is under way thus improving the competitiveness of fiber-based packaging materials and enabling enhanced packaging solutions [1]. There is a clear need to upgrade the existing materials and thin inorganic coatings are an interesting way to create high-performance materials for food packages.

Here we demonstrate significantly enhanced barrier properties towards oxygen, water vapor and aromas for various polymer-coated papers and paperboards as achieved by coating them with a thin conformal aluminum oxide layer grown by the atomic layer deposition (ALD) technique. 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 pinhole-free inorganic films that are uniform in thickness even deep inside pores, trenches and cavities of various dimensions. The other advantages of ALD include low impurity content and mild deposition conditions in terms of temperature and pressure. There is a wide range of ALD-grown materials and commercial applications, from catalysts to electroluminescent displays in microelectronics and beyond [2–4].

The ALD technique has been used to produce gas-diffusion barriers on polymers [5–7]. Water-vapor transmission rates of the order of 1×10^{-3} g/m²/day were reported for less than 25-nm thick Al₂O₃ depositions on polymers [5]. In addition, Park et al. [7] reported a water-vapor transmission rate value of 0.03 g/m²/day at 38 °C and 100% relative humidity for an ALD-grown Al₂O₃ barrier that was 30 nm thick and deposited on both sides of a poly(ethersulfone) substrate, whereas Garcia et al. [6] showed that a 25-nm thick ALD-Al₂O₃ barrier films on poly(ethylene naphthalate) substrates can have a water-vapor transmission rate less than 1×10^{-5} g/m²/day. These results are, however, only partly comparable with our results because some of our substrates are biodegradable. Our aim was to study biodegradable and recyclable substrates and compare the results to those obtained for conventional synthetic polymer substrates used as gas-diffusion barriers. There are no previous studies concerning less than 100-nm thick ALD-grown Al₂O₃ layers on biodegradable polymers or fiber-based substrates coated with synthetic or biopolymers.

2. Experimental details

A variety of uncoated papers, polymer-coated boards and papers, and plain polymer films as summarized in Table 1 were used as

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Table 1
Commercial substrates used in the ALD- Al_2O_3 deposition tests.

Code	Description
P(PIG)	Pigment-coated and calendered high gloss paper 60 g/m ²
P(LDPE)	Polyethylene (LDPE) coated paper
P(UNC)	Commercial uncoated copy paper 80 g/m ²
B(PE)	Polyethylene-coated (15 g/m ²) board
B(PLA)	Poly(lactic acid (PLA) coated (35 g/m ²) board
PEN	Polyethylene naphthalene (PEN) film, 50 μm
PP	Polypropylene film, 30 μm
PET	Polyester (PET) film, 50 μm
PLA	PLA film, 25 μm

substrates for the Al_2O_3 depositions. Al_2O_3 coatings of different thicknesses (of 5, 25, 50, 100 and 900 nm) were deposited at 80 °C using a commercial ALD TFS 500 reactor manufactured by Beneq Ltd., Finland. Trimethylaluminum (TMA, Sigma-Aldrich, 98% purity) and water were used as precursors for aluminum and oxygen, respectively. The precursors were introduced in the reactor in alternate pulses, separated by an inert N_2 gas pulse such that one ALD cycle comprised the following four process steps: (i) TMA pulse, (ii) N_2 purge pulse, (iii) water pulse, and (iv) N_2 purge pulse [8]. The substrates were ca. 10 cm*10 cm in size, and they were coated on one side only. This was achieved by taping the substrate on the sides so that the gas flow could only reach one side of the substrate. The targeted coating thicknesses were produced according to the TFS 500 reactor process parameters based on the thicknesses determined for Al_2O_3 films on a silicon wafer by means of ellipsometry with an accuracy of ± 0.5 nm.

Thermogravimetric (TG) analysis was performed for all substrate materials except P(PIG) and P(UNC) to reveal the thermal behavior and the limitations of different polymer coatings to be used as substrates in ALD depositions. The TG experiments were performed in both air and nitrogen atmospheres with a heating rate of 10 °C/min.

Selected samples, *i.e.* P(UNC), P(PIG), B(PE) and B(PLA), were characterized with X-ray photoelectron spectroscopy (XPS; KRATOS AXIS 165) for the surface chemistry and surface distributions and by scanning electron microscopy (SEM; Hitachi S-3400 N VP-SEM, operating voltage 15 keV) for the microstructure. In the XPS analysis monochromatic Al K α (12.5 kV, 8 mA) radiation at 100 W was used. Wide binding energy range spectra (0–1100 eV) were recorded using 80 eV pass energy and 1 eV step. The high-resolution spectra of C 1s and O 1s regions were also recorded, using 20 eV pass energy and 0.1 eV. The area measured was approximately 1 mm² while the analysis varies from 2 to 10 nm, depending on the element and on the sample material. Also an atomic force microscopy (AFM; Nanoscope III a Multimode scanning probe microscope, Digital Instruments Inc.) image from the PEN film (PEN) was taken to demonstrate the topography of the ALD-treated sample surface.

The oxygen transmission rates (OTR) were measured using humid gases with a Mocon OXTRAN equipment and expressed as cm³/m²/10⁵ Pa/day. The measurements were performed at 23 °C and at 50–60% relative humidity. The water-vapor transmission rates (WVTR) were measured from flat samples according to the modified gravimetric methods ISO 2528:1995 and SCAN P 22:68 and were expressed as g/m²/day. The test conditions were 23 °C and 75% relative humidity. KCL AromaBar equipment was used for evaluating the aroma barrier properties. Details of the test cell and the method used have been described elsewhere [9].

3. Results and discussion

3.1. Thermal stability of the biopolymer-coated substrate materials

Thermogravimetric analyses were performed both in air and nitrogen atmospheres to reveal the thermal behavior and the limitations of different polymers and polymer-coated papers and boards to be used

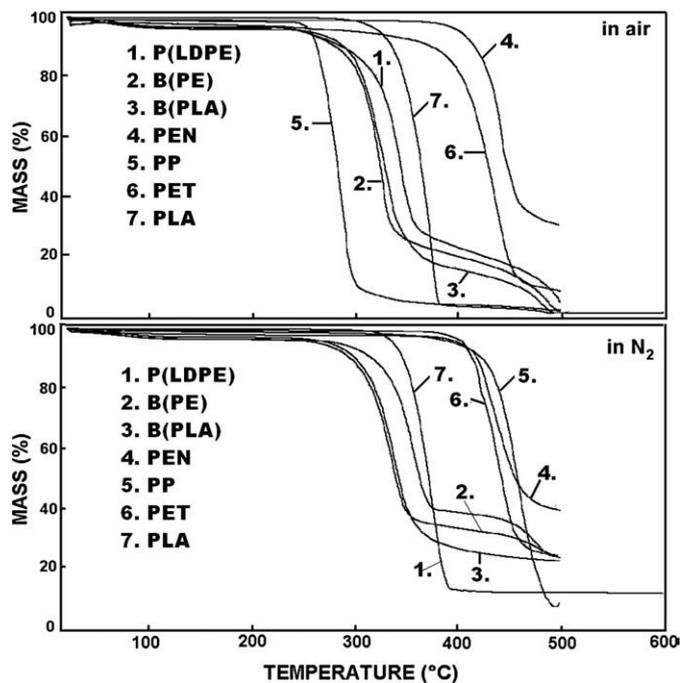


Fig. 1. TG curves recorded for seven different substrate materials in air and nitrogen atmospheres.

as substrates in the ALD depositions. The resultant TG curves are presented in Fig. 1. All the substrate materials investigated were found to behave quite similarly. No significant water removal occurred at low temperatures, instead the materials decomposed in an essentially single, sharp step at temperatures ranging from 300 to 450 °C. Except for PEN and PET, decomposition was practically complete by 450 °C in air, whereas in nitrogen the decomposition was more incomplete and shifted to higher temperatures. Most importantly, the TG measurements confirmed that the materials tested do not degrade thermally at temperatures employed in low-temperature ALD experiments, *i.e.* below ~150 °C.

3.2. Characterization of the Al_2O_3 coatings

XPS provides two independent means of surface coverage analysis. In the conventional approach, quantitative analysis based on XPS peak

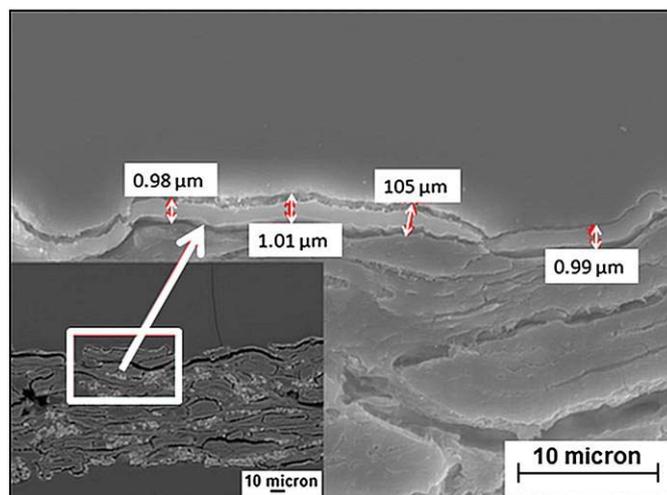


Fig. 2. A cross-cut SEM image from a paper sample P(UNC) with a 900-nm thick ALD-grown layer of Al_2O_3 on top of it.

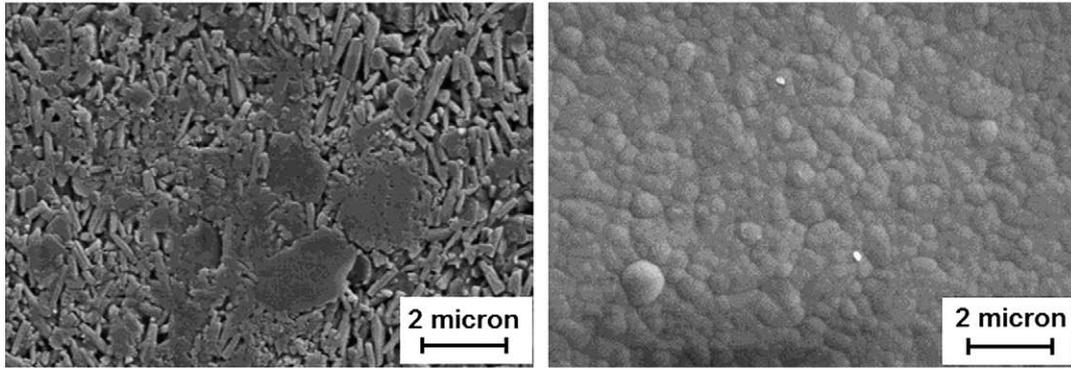


Fig. 3. SEM images of pigment-coated paper surface of P(PIG) as such (left) and with a 900-nm thick ALD-grown Al_2O_3 layer on top of it (right).

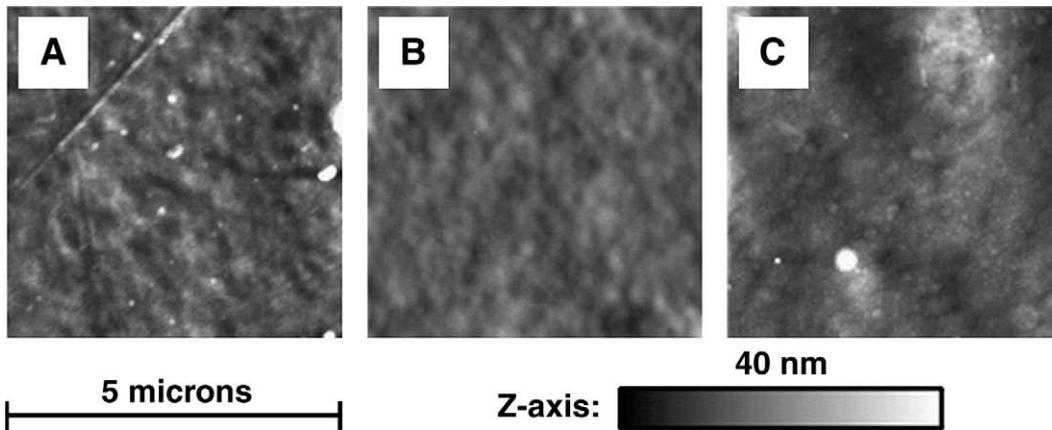


Fig. 4. AFM topographic images of A) a pure polyethylene naphthalene film (PEN) with B) a 100-nm thick and C) a 900-nm thick ALD-grown Al_2O_3 layer on top of it.

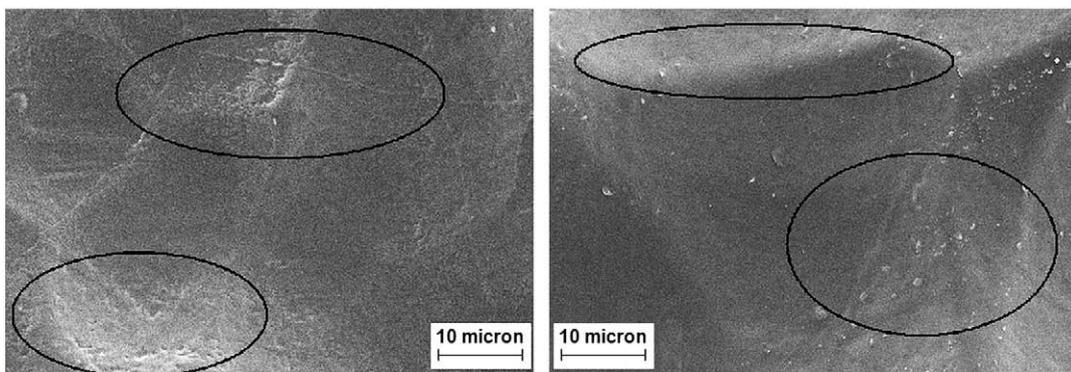


Fig. 5. SEM images of polyethylene-coated board B(PE) (left) and polylactic acid-coated board B(PLA) (right) with a 20-nm thick ALD-grown Al_2O_3 layer on top of it.

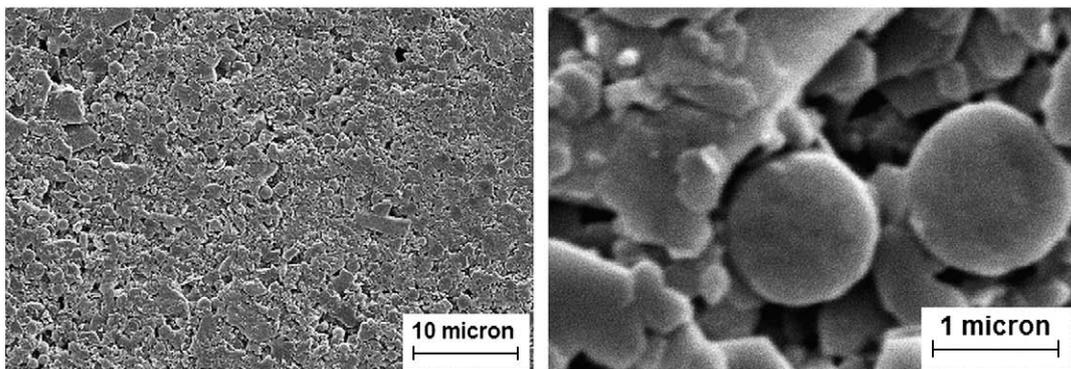


Fig. 6. SEM images of coated paper P(PIG) with magnification from the deposited 900-nm layer of Al_2O_3 .

intensities is used. In addition to this, surface depth distributions may be evaluated from the spectral backgrounds tailing each peak, according to the approach formulated by Tougaard et al. [10–13]. This latter method is especially well suited for thin film studies, because it differentiates homogeneous films from films with loopholes, and because it gives information of surface coverage up to three times the inelastic mean free path (IMFP) of the photoelectron signal studied.

Here, the XPS analyses were performed on samples with a 25-nm thick aluminum oxide coating, in order to evaluate the chemistry and the coverage of the ALD-deposited coating. In the case of even, 25-nm thick surface film, the sample should behave as a semi-infinite bulk material. This means that there should be no signal from the substrate, neither as peaks nor as changes in the spectral background. Thus, XPS data of a uniform surface film should be similar to the respective bulk material (including peaks and the spectral backgrounds tailing them).

In this case, coverage analysis using elements was not optimal, since the surface contamination (unavoidable in air-exposed metal oxide surfaces) and substrate both contained carbon. However, the carbon signal detected was chemically similar to typical surface contamination (but differed markedly from substrates). Furthermore, there was no inelastic background tailing the carbon signal, indicating that the carbon observed originated just from the outmost surface and not from the bulk. In addition to these, the spectral background shapes of aluminum and oxygen were both indicative of uniform, homogeneous depth distributions.

Put together, XPS data confirmed that the substrates *i.e.* P(PIG), B(PE) and B(PLA), had been covered quite efficiently by a homogenous ALD layer of Al₂O₃, within the detection depth of XPS (2–10 nm).

SEM images were taken to inspect the cross cuts and surfaces of the Al₂O₃-coated samples. In Fig. 2, a cross-cut SEM image taken from a paper sample P(UNC) with a 900-nm ALD-grown layer of Al₂O₃ on top of it is shown. The deposited Al₂O₃ layer is readily observed and found to be highly conformal and homogeneous in thickness. With porous surfaces, such as the surface of our uncoated paper sample P(UNC), Al₂O₃ enters also into the pores of the paper.

Fig. 3 shows SEM images of a pigment-coated paper P(PIG) before and after the deposition of a 900-nm thick Al₂O₃ layer. The initial topography of the substrate surface has no substantial effect on the resultant Al₂O₃ surface. That is, the barrier layer is nearly complete as it fills or overlays the pores. Very similar surface structures have been observed also for other materials studied here.

Fig. 4 presents AFM images of a pure polyethylene naphthalene film and the same film with 100-nm and 900-nm thick Al₂O₃ layers on top of it. The surface looks rather similar to the pigment-coated paper surface with a similar Al₂O₃ coating (Fig. 3). Both pigment-coated paper and PEN surfaces with a thick Al₂O₃ coating appear granular. The surface of a pure PEN film shows also a fine structure in the nm scale (rms roughness 4.5 nm). A 100-nm thick Al₂O₃ layer (rms 2.94 nm) cannot totally hide the surface features, but with a 900-nm thick layer (rms 4.89 nm) the granularity is obvious. The granular surfaces could be due to the uneven surface properties and hydrophobicity of the substrate. Our hypothesis is that the unevenness and hydrophobicity influence the water pulse in the ALD cycle. The chemical variations of the polymer as well as the variations in crystallinity of the polymer may cause the ALD-Al₂O₃ layer

Table 2

Oxygen transmission rates (cm³/m²/10⁵ Pa/day) of non-coated and Al₂O₃-coated (with various Al₂O₃-layer thicknesses) samples.

Code	Non-coated	25 nm	50 nm	100 nm
P(PIG)	>20,000	>20,000	>20,000	>20,000
B(PE)	>20,000	6650	818	3700
B(PLA)	3150	49	121	513
PP	1250	170	109	103
PET	24	11	12	10
PLA	315	44	32	57

Table 3

Water-vapor transmission rates (g/m²/day) of non-coated and 50-nm Al₂O₃-coated samples.

Code	Non-coated	50 nm
P(LDPE)	5.4	3.1
B(PE)	8.5	4.6
B(PLA)	131	14
PEN	0.9	0.6
PLA	93	3.3

to grow unevenly. Pretreatment procedures could solve both of these problems.

The polyethylene-coated and polylactic acid-coated board samples, B(PE) and B(PLA), in Fig. 5 are coated with a 20-nm thick Al₂O₃ layer. Small structural features (marked in the figure) can be observed in the sample surfaces in the SEM images. The sample surfaces seem to be grainy. The polymer surface is probably partly heterogeneous. This may have an influence on the growth of the Al₂O₃ layer, especially in the beginning of the ALD process. In addition, if the sample is highly porous, thin Al₂O₃ layers cannot totally fill the pores, as indicated in Fig. 6 for the coated paper P(PIG).

3.3. Barrier properties

Oxygen transmission rates were measured by positioning the Al₂O₃-coated side of the sample facing the carrier gas stream. The thus obtained OTR values are presented in Table 2. From Table 2, it is clearly seen that the ALD-Al₂O₃ treatment has improved the oxygen barrier properties of the materials tested here. However, the OTR value does not change linearly with the thickness of the deposited Al₂O₃ layer. In the cases of the polymer-coated paper and board substrates, B(PE) and B(PLA), and the plain polylactic acid film sample PLA, a higher OTR value is obtained for a 100-nm thick Al₂O₃ coating than for the thinner layers. For the polypropylene film substrate PP, on the other hand, the OTR value decreases with increasing thickness of the Al₂O₃ layer. With the polyester film substrate PET the thinnest Al₂O₃ layer seems to improve the barrier properties as much as the thicker layers. The varying responses could be due to *e.g.* differences between the surface roughnesses of the polymers. An excessively thick layer may cause cracking, which in turn impairs the barrier properties. The OTR value for the pigment-coated paper P(PIG) remains very high, even for the Al₂O₃-layer thickness of 100 nm. In this case the substrate surface contained cracks and the pores were probably not filled with a thick ALD-Al₂O₃ layer.

The water-vapor transmission rate measurements were carried out for substrates coated with a 50-nm thick Al₂O₃ layer, and for each material three parallel samples were measured. The WVTR results are presented in Table 3. Similarly to the OTR values, the positive effect of a thin Al₂O₃ layer on the WVTR value is evident. Especially the polylactic acid-coated board and the polylactic acid film samples B(PLA) and PLA are found to experience a significant improvement in the WVTR as achieved through the ALD-grown Al₂O₃ layer.

The aroma barrier properties were measured only for one substrate material, polyethylene-coated paper P(LDPE). Results are shown in Table 4. Although the diffusion coefficient decreases more

Table 4

Diffusion coefficients (10⁻¹⁵m²/s) for different aromas measured for the P(LDPE) sample before and after coating it with a 50-nm Al₂O₃ layer.

Code	coated	50 nm
Isoamyl acetate	9.1	3.6
D-Limonene	15.8	8.7
cis-3-hexenol	7.6	3.6
r-Carvone	9.9	5.2

than 50% of the original value the aroma barrier properties are considered to be of medium level only. The improvement is not as dramatic as expected. This result is in line with the results from the WVTR measurements for the same substrate material.

4. Conclusions

Aluminum oxide films with thicknesses ranging from few nanometers to one-micron scale were grown using the ALD technique at low temperature on polymer films and on papers and boards coated with polymers. XPS and SEM results indicated that even the thinnest films provided a good coverage over the surface features of the various porous and non-porous substrate materials investigated. However, there were also signs of some graininess in nanometer scale which may be a disturbance. Even without being optimized, the barrier properties of the substrate materials studied were improved significantly – especially for oxygen and water-vapor diffusion – upon coating the materials with a thin ALD-deposited layer of Al_2O_3 .

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