

PUBLICATION IV

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Effect of corona pre-treatment on the performance of gas barrier layers applied by atomic layer deposition onto polymer-coated paperboard

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ABSTRACT

The effect of corona pre-treatment on the performance of Al₂O₃ and SiO₂ gas barrier layers applied by atomic layer deposition onto polymer-coated paperboards was studied. Both polyethylene and polylactide coated paperboards were corona treated prior to ALD. Corona treatment increased surface energies of the paperboard substrates, and this effect was still observed after several days. Al₂O₃ and SiO₂ films were grown on top of the polymer coatings at temperature of 100 °C using the atomic layer deposition (ALD) technique. For SiO₂ depositions a new precursor, bis(diethylamido) silane, was used. The positive effect of the corona pre-treatment on the barrier properties of the polymer-coated paperboards with the ALD-grown layers was more significant with polyethylene coated paperboard and with thin deposited layers (shorter ALD process). SiO₂ performed similarly to Al₂O₃ with the PE coated board when it comes to the oxygen barrier, while the performance of SiO₂ with the biopolymer-coated board was more moderate. The effect of corona pre-treatment was negligible or even negative with the biopolymer-coated board. The ALD film growth and the effect of corona treatment on different substrates require further investigation.

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1. Introduction

The tightened requirements for the quality and safety of various food items have increased the need for better packaging materials. 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. Most of the studies have concerned polyethylene, ethyl vinyl alcohol and poly(ethylene terephthalate) but in recent years, owing to increased impact of environmental issues, the replacement of fossil-based raw materials with bio-based materials has become important.

Many biopolymers are hygroscopic materials, meaning that they will 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 [2]. In order to prevent

the phenomenon, thin glass-like SiO_x coatings have been utilized to improve the gas barrier properties of moisture sensitive materials [3,4]. Furthermore, 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.

Atomic layer deposition (ALD) technique is a surface controlled layer-by-layer thin film deposition process based on self-terminating gas–solid reactions. It 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. In our previous work thin Al₂O₃ coatings were deposited by the ALD technique at low temperature on various polymer-coated papers and boards and plain polymer films [5]. The work demonstrated that such ALD-grown Al₂O₃ coatings efficiently enhanced the gas-diffusion barrier performance of the studied materials towards oxygen, water vapor and aromas. We also have demonstrated that ALD is a recommended thin film deposition technique when making extremely thin (25 nm) barrier coatings from Al₂O₃ to temperature sensitive fiber-based materials [6].

Despite the promising results, improvement in barrier performance towards gases is still needed in order to create barrier coatings suitable for demanding packaging purposes. One route

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towards improved barrier performance could be to pre-treat the substrate before the ALD. The surface chemistry of the substrate may affect the ALD deposition, especially the initial formation of the monolayers due to e.g. different amounts of hydrogen-bonded water on the surfaces. Based on our hypothesis, pre-treating the surface could even out the surface chemistry and enhance the uniformity of the ALD layer on polymeric coatings and thus improve the barrier properties, especially those obtained with thin ALD-grown coatings. Polymer films are often chemically inert, non-porous, and have low surface energy. This causes surfaces to be non-receptive to wetting and bonding with e.g. aqueous coatings. Corona treated films exhibit a higher surface energy crucial for producing high quality coated products.

Pre-treating substrates with corona discharge is a widely used method for polyolefin films [7]. Corona treatment is an electrical process which utilizes ionized air converting the substrate surface from non-polar to polar state. The surface is bombarded with ozone, oxygen and free radicals of oxygen and this enables the oxidation of the surface which increases the surface energy. Corona treatment has been found to increase oxygen content and carbon–oxygen functionalities on low-density polyethylene, while the effect on more polar ethylene methyl acrylate copolymer was marginal [8]. Due to the fact that there are significantly less polar functional groups on polyethylene (PE) than on polylactide (PLA) we assumed that the effect of corona treatment would be more profound with PE. In addition to oxidation, the effect of corona on the polymer surface can be due to cross-linking and removal of low molecular weight contaminants [8,9], changing surface micro-roughness and morphology [8–10], and formation of electret [8,11]. However, no significant changes in roughness values have been observed with corona treatment in earlier studies [12–14]. Changes in polymer morphology cannot be ruled out.

The aim of the present work was to study the influence of corona pre-treatment to the oxygen and water vapor barrier performance of polymer-coated boards additionally coated with Al_2O_3 and SiO_2 by the ALD. In SiO_2 depositions, a new precursor (bis(diethylamido) silane) was used. Use of this precursor has not been previously published in relation with barrier coatings. SiO_2 has been grown by the ALD using compounds such as $\text{Si}(\text{NCO})_4$, and $\text{N}(\text{C}_2\text{H}_5)_3$ as precursors [15]. Deposition of SiO_2 using SiCl_4 and H_2O as precursors has also been described [16], as well as dichloro silane (SiH_2Cl_2) and O_3 [17]. However, the problem with these precursors is the relatively high deposition temperatures which cannot be used with heat sensitive materials, such as polymer-coated boards.

2. Experimental details

Commercial paperboards with both synthetic low-density polyethylene (B(PE): board 210 g/m^2 ; coating 15 g/m^2) and bio-based polylactide (B(PLA); board 310 g/m^2 ; coating 35 g/m^2) coatings were used as substrates. The corona pre-treatment was performed at VTT with a corona treatment unit from Vetaphone (type: CP1C MKII, 2.0 kW, TF-415). The speed of the substrate was 500 mm/min and the power output of the corona treatment was 50 Wmin/m^2 . This is a widely used treatment unit for plastics [18].

ALD coatings were deposited at 100°C using a commercial SUNALE™ R-series reactor manufactured by Picosun Oy, Finland targeting at coating thicknesses of 25 and 50 nm. The general procedure of ALD- Al_2O_3 depositions has been reported previously elsewhere [6]. The ALD precursors for 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. For Al_2O_3 depositions the precursor pulses lasted 0.1 s and the purges 5 s.

The procedure for SiO_2 depositions was based on the earlier study of Dussarrat et al. [19]. For SiO_2 depositions the precursors were bis(diethylamido) silane (SAFC Hitech, electronic grade purity) and ozone (20 vol%) produced from oxygen (99.9999%). Surface OH^- -groups have different reactivity towards Al_2O_3 and SiO_2 . In order to initiate the SiO_2 film growth, a thin ($\sim 2\text{ nm}$) layer of Al_2O_3 was first deposited from TMA and water. For Al_2O_3 depositions the precursor pulses lasted 0.1 s and the purges for 4 s, respectively. For SiO_2 depositions the precursor pulses lasted 1 s and the purges for 5 s.

The resultant film growth rates and actual film thicknesses on the polymer-coated boards could not be directly measured. Instead, the coating thicknesses were produced according to the reactor process parameters and compared to the thickness of Al_2O_3 and SiO_2 on a silicon wafer analyzed with a Nanospec AFT4150 reflectometer. The film growth rates for ALD were estimated to be ca 1.1 \AA/cycle for TMA- H_2O and silane- O_3 0.085 \AA/cycle . Due to the different polarities and functional groups of the PE and PLA surfaces the actual growth rates on the polymer-coated board substrates may somewhat deviate from those determined for the ALD coating on silicon wafer [20,21]. Although the aim was to deposit only the polymer-coated side of the substrate, film growth also on the uncoated side could not be totally prevented.

Contact angle (CA) and surface energy (SE) measurements were made directly after the corona pre-treatment and repeated 7 days after the pre-treatment. These measurements were carried out in order to study the decrease in surface energy during a certain time period. The measurements were made with KSV CAM 200 Optical Contact Angle Meter in a controlled atmosphere (RH 50%, temperature 23°C) and were expressed as $^\circ$ for contact angle and mN/m for surface energy. The probe liquids used were H_2O and di-iodomethane (CH_2I_2). Results are given as an average of three parallel measurements. The surface energy values, including dispersive and polar components, were calculated from the contact angle data using the OWRK (ext. Fowles) theory. The values of contact angles were calculated at the time of 1 s from the moment the drop contacts the surface.

The oxygen transmission rate (OTR) was measured from two to three parallel samples using humid gases at room temperature (23°C) with Systech M8001 and Mocon OXTRAN equipment and expressed as $\text{cm}^3/\text{m}^2/10^5\text{ Pa/day}$. The results from the two OTR equipments were roughly the same so the results from two different equipments may be compared. The water vapor transmission rate (WVTR) was measured from three to five parallel flat samples according to the modified gravimetric methods ISO 2528:1995 and SCAN P 22:68 and was expressed as $\text{g}/\text{m}^2/\text{day}$. Test conditions were 23°C and 75% relative humidity.

3. Results and discussion

3.1. Surface energies of the polymer-coated substrate materials

As described in our previous work [6], the surface topographies of the substrates B(PE) and B(PLA) vary greatly from each other. 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). 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 Al_2O_3 and SiO_2 during parallel ALD treatments. Compared to the smoother B(PLA) substrate, the B(PE) substrate has larger specific surface area and accordingly larger concentration of surface sites to accommodate larger amounts molecules upon the ALD depositions.

Table 1
Contact angle with water (CA) and surface energy (SE) values (γ^d , γ^p , γ^s) of pristine substrates directly after the corona pre-treatment and after 7 days from the pre-treatment.

Sample	Directly after pre-treatments				Seven days after pre-treatments			
	CA	γ^d	γ^p	γ^s	CA	γ^d	γ^p	γ^s
B(PE) untreated	90	36.7	3.8	40.5	90	36.7	3.8	40.5
B(PE) corona treated	67	43.5	7.6	51.0	71	41.2	6.4	47.7
B(PLA) untreated	71	40.1	7.7	47.8	71	40.1	7.7	47.8
B(PLA) corona treated	62	42.7	10.4	53.1	67	42.2	8.0	50.2

The results from the contact angle measurements with water and surface energy analyses are presented in Table 1. The total value of surface energy (γ^s) consists of dispersive (γ^d) and polar (γ^p) components. The latter measures the increase in polarity on the surface. The polar component is our main interest because it indicates the density of polar groups on the surface.

Results showed that the contact angle values of both B(PE) and B(PLA) changed after the corona pre-treatment making the surfaces more hydrophilic. The change was greater for B(PE) than for B(PLA). In addition, for B(PE) the contact angle remained approximately similar for 7 days. For B(PLA) the influence of corona pre-treatment was minor and after 7 days the contact angle with water was almost the same than before the pre-treatment. The surface energy values also increased when corona pre-treatment was applied. The results imply that the amount of polar groups at the surface increased. The effect was greater for B(PE) than for B(PLA). This can be explained by the different behavior of the chemical bonds in these polymers, PE and PLA, and the capability of the polymers to form additional oxygen containing functional surface groups. For both of the substrates the surface energy values remained at higher level after 7 days.

We also applied significantly lower corona treatment ($<10 \text{ Wmin/m}^2$) to the same samples with a smaller and simple corona unit, and Enercon Industries performed atmospheric plasma treatment to the samples with an optimized gas mixture. Plasma treatment is interesting due to lower tendency of the base polymer to degrade during the treatment without pin-holing and backside treatment. Plasma treatment also allows wider adjustment of surface properties by using different gases or gas mixtures. Unfortunately, no clear effect of these pre-treatments could be detected on contact angles or surface energy. The reason for the poor result with the plasma treatment could be the time delay of several days between the treatment and the measurement.

3.2. Barrier properties

Oxygen transmission rates (OTR) were measured in a way that the ALD deposited side of the sample faced the oxygen stream. The results are presented in Table 2.

Table 2
Oxygen transmission rates ($\text{cm}^3/\text{m}^2/10^5 \text{ Pa/day}$) of pure B(PE) and B(PLA) substrates and Al_2O_3 or SiO_2 coated substrates with and without of pre-treatment. The results are given as average \pm standard deviation of two to three parallel measurements.

Sample	Untreated	Corona treated
B(PE) uncoated	7900 \pm 1600	5700 \pm 140
B(PE) + 25 nm Al_2O_3	6700 \pm 2500	1400 \pm 70
B(PE) + 50 nm Al_2O_3	2700 \pm 400	1800 \pm 200
B(PE) + 25 nm SiO_2	5050 \pm 1300	2000 \pm 140
B(PE) + 50 nm SiO_2	2100 \pm 900	2500 \pm 140
B(PLA) uncoated	420 \pm 10	328 \pm 1.0
B(PLA) + 25 nm Al_2O_3	20 \pm 3	17 \pm 5
B(PLA) + 50 nm Al_2O_3	60 \pm 5	80 \pm 50
B(PLA) + 25 nm SiO_2	360 \pm 5	250 \pm 10
B(PLA) + 50 nm SiO_2	20 \pm 2	27 \pm 5

Corona treatment improved the oxygen barrier properties of the substrates as such probably due to the surface cross-linking caused by the relatively strong pre-treatment. Cross-linking of base polymer can also decrease diffusion of precursors into the polymer matrix. The influence of the corona treatment was greater for B(PE) than for B(PLA). Corona treatment seems also to lead to more even ALD-grown layers due to smaller standard deviation with corona pre-treated samples.

For B(PE), without the corona pre-treatment, the thicker (50 nm) Al_2O_3 layer, i.e. the longer ALD process, resulted in better barrier properties than the thinner (25 nm) layer, i.e. the shorter ALD process. However, the situation was different after corona treatment; better oxygen barrier properties were obtained already with 25 nm Al_2O_3 layers. For SiO_2 depositions, the barrier properties were most improved when a 50 nm SiO_2 layer was deposited onto substrate but after the corona pre-treatment the thinner (25 nm) layers resulted in larger improvement.

When B(PLA) was used as a substrate and Al_2O_3 layers were deposited on the substrate without corona pre-treatment, a 25 nm Al_2O_3 layer improved the properties more than a thicker (50 nm) layer. After the pre-treatment, the properties of the 25 nm Al_2O_3 layer remain practically at the same good level. The barrier performance did not improve further with the 50 nm Al_2O_3 layer, which could be due to the cracking behavior of thick ALD films [5]. However, for SiO_2 depositions, the barrier properties improved most when a 50 nm SiO_2 layer was deposited onto substrate and the properties were further improved after corona pre-treatment. For B(PE) and B(PLA), in general, the best barrier properties towards oxygen were obtained with a 25-nm Al_2O_3 layer on top of corona pre-treated substrates.

The WVTR results are presented in Table 3. The results show that the corona pre-treatment only slightly improved the water vapor barrier properties for both of the uncoated substrates. For B(PE), both with and without the corona pre-treatment, the 50 nm Al_2O_3 layers resulted in better barrier properties than the 25 nm Al_2O_3 layers. The values with and without corona pre-treatment are close to each other when taking into account the statistical scattering. With SiO_2 depositions on B(PE), the barrier properties were at the same level with both film thicknesses as with the Al_2O_3 layers. However, the corona treatment improved the WVTR of the

Table 3
Water vapor transmission rates ($\text{g}/\text{m}^2/\text{day}$) of pure B(PE) and B(PLA) substrates and Al_2O_3 or SiO_2 coated substrates with and without of pre-treatment. The results are given as average \pm standard deviation of three to five parallel measurements.

Sample	Untreated	Corona treated
B(PE) uncoated	7.0 \pm 0.9	6.2 \pm 0.4
B(PE) + 25 nm Al_2O_3	6.9 \pm 0.1	6.1 \pm 1.1
B(PE) + 50 nm Al_2O_3	2.0 \pm 0.5	4.6 \pm 1.6
B(PE) + 25 nm SiO_2	6.3 \pm 0.3	2.9 \pm 0.3
B(PE) + 50 nm SiO_2	6.5 \pm 1.0	7.0 \pm 0.4
B(PLA) uncoated	64.9 \pm 1.6	60.5 \pm 0.4
B(PLA) + 25 nm Al_2O_3	1.4 \pm 0.2	5.7 \pm 3.8
B(PLA) + 50 nm Al_2O_3	1.8 \pm 0.5	13.2 \pm 5.9
B(PLA) + 25 nm SiO_2	48.1 \pm 1.8	42.2 \pm 1.1
B(PLA) + 50 nm SiO_2	41.5 \pm 5.3	41.9 \pm 2.7

25 nm SiO₂ layer. This could be due to a more even Al₂O₃ layer under the SiO₂ layer. With B(PLA) the best WVTR was obtained with Al₂O₃ without the corona pre-treatment. Corona treatment impaired the WVTR, although the values were better than those obtained with SiO₂ on the same substrate. Similarly to the OTR, the WVTR of the 50 nm Al₂O₃ layer increased more than with the thinner layer. The negative effect of corona pre-treatment on the performance of B(PLA) could be due to uneven or too excessive treatment.

When Al₂O₃ was applied on B(PLA) without corona pre-treatment, the 25 nm Al₂O₃ layer improved the oxygen barrier properties more than the 50 nm layer. Corona treatment did not alter the situation. When SiO₂ was applied on B(PLA) without corona pre-treatment the barrier properties were slightly better with the thicker (50 nm) SiO₂ layer. After the pre-treatment, the properties of the 25 nm SiO₂ layer were improved, as the properties of the thicker layer remained the same. The cracking of thicker ALD layers may affect also the water vapor barrier [5]. The effect of corona treatment on water vapor barrier properties of the studied substrates were not as clear as it was for oxygen barrier properties for e.g. B(PE). It is evident that in order to clarify this, more investigation is needed. 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 result in a poor quality ALD-grown coating.

Neither the low corona nor the atmospheric plasma treatment had an unambiguous effect on the barrier properties. In the case of plasma treatment this might be due to the time delay of several days between the treatment and the ALD test.

The decrease in the barrier properties with increasing ALD layer thickness in some cases is in line with our initial studies [5]. The same phenomenon has been detected also with other thin deposition methods, such as vacuum sputtering [6]. The ALD film thickness must thus be optimized for each substrate and process parameters separately. The effect of corona treatment was assumed to be most obvious when aiming at thin ALD films due to the different initial film growth between untreated and treated polymer surfaces. This study utilized the ALD process with two different number of process cycles.

Due to the different polarities and type/density of functional groups of the untreated and treated polymer surfaces the nucleation and the initial film growth may somewhat deviate from each other and from that determined for the ALD-Al₂O₃ coating on silicon wafer [20–22]. The reason for the different properties between the untreated and corona treated and ALD deposited samples could thus be dissimilar film thickness and evenness of the grown film. Secondly, diffusion of precursors into and out of the polymer surface [22] is likely affected both by the polymer type and the pre-treatment, especially during the initial stages of film growth. Cross-linking of the polymer surface during corona treatment could decrease diffusion of precursors into the polymer, thus making the interface between the polymer and the ALD film sharper. The interface between e.g. polyethylene and Al₂O₃ has been found problematic in other studies [23]. In spite of a probably more uniform ALD film on the corona treated samples, the interfacial tension could become higher with thick ALD films causing cracking. Thirdly, corona treatment can increase the roughness of polymer surfaces. However, this is not very likely as stated earlier. Clearly, the ALD film growth on different substrates needs further investigation.

The results with e.g. PLA coated board would indicate that the SiO₂ film is more polar and the structure more open than the Al₂O₃ film. The open structure would explain the need for a thicker SiO₂ layer for improved oxygen barrier. However, even thick film of this

material cannot decrease water vapor barrier significantly due to possible swelling. The problem with SiO₂ ALD is in some cases formation of salt [22]. It is well known that oxygen and water vapor barrier properties do not necessary correlate. With a dense polar polymer, such as ethylene vinyl alcohol copolymer, oxygen barrier can be good when dry, but the polymer structure swells at humid conditions.

4. Conclusions

The effect of corona pre-treatment on the oxygen and water vapor barrier properties of Al₂O₃ or SiO₂ layers applied by the ALD technique onto polymer-coated paperboard was studied. Corona treatment was performed for polyethylene and polylactide coated boards. Al₂O₃ and SiO₂ layers were then successfully deposited at low temperature on these fiber-based substrates. For SiO₂ depositions a new precursor, bis(diethylamido) silane, was used. Substrates that had been corona surface treated exhibited a higher surface energy and the effect of the treatment lasted for several days at the substrate surface. The positive effect of the corona pre-treatment of the polymer-coated boards on the barrier properties after the ALD deposition was more significant with the polyethylene coated paperboard and with thin deposited layers, i.e. the short ALD process. This supports our hypothesis concerning more favorable substrate surface chemistry after corona pre-treatment, especially with thin deposited layers. In addition, cross-linking of polymer surface layer may decrease diffusion of precursors into the polymer matrix. These are more important than the less likely increase in surface roughness during the corona pre-treatment. SiO₂ performed similarly to Al₂O₃ with the PE coated board when it comes to the oxygen barrier, while performance of SiO₂ with the biopolymer-coated board was more moderate. Corona treatment also evened out the surface properties of some samples. However, the effect of corona pre-treatment was negligible or even negative on the water vapor barrier, especially with the polylactide coated board. Clearly, the ALD film growth and the effect of corona pre-treatment on different substrates need further investigation.

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