RESEARCH REPORT

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Atomic layer deposition onto polymer surfaces

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Summary

The goal was to study polymer films and coated paperboard as base substrates for atomic layer deposition (ALD), to understand the parameters affecting layer growth and functional properties, to characterize thin layers, and to assess their safety and sustainability.

Barrier properties of most polymer films studied were improved by Al_2O_3 thin layers. The relative improvement was the most significant with cellulose and polyester films, while certain plastic additives completely prevented thin layer growth. Polymer pre-coatings on fiber-webs have to be smooth and have good film forming properties.

Layer growth starts by sorption of precursors onto and into the polymer surface followed by chemical reactions with the polar oxygen groups of the polymer and a possible formation of an interphase. This is followed by cluster formation and growth through clusters. The amount of oxide needed to cover the polymer depends on its' surface chemistry. Surface chemistry of polymer film has an impact on the layer growth and final functional properties. Polymer pre-treatments prior to the ALD can be used to improve the barrier properties. Ozone can activate difficult surfaces, and the barrier properties can be adjusted by choosing the oxygen source. In addition, deposition temperature should be as high as possible.

Mechanical properties of oxide layers were improved by combining thinner oxide and inorganic-organic hybrid layers into a nanolaminate. In addition, a contact between the oxide layers and the bacteria promoted antimicrobial activity.

Uniform Al_2O_3 barrier layers do not seem to fall under the EU's definition of nanomaterial. Migration of Al_2O_3 to food simulants was low. However, ALD coated polymers require a top layer to protect the oxide layer from stresses, to prevent dissolution and to act as a sealant.

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Preface

This report contains the main results obtained at VTT during the time period of 1.8.2010-31.8.2013 within the Roll-to-roll atomic layer deposition process development (RRALD) project. We want to thank the Finnish Funding Agency for Technology and Innovation, Bemis Valkeakoski, Saarioinen and StoraEnso for their funding.

RRALD included three parallel projects to develop a roll-to-roll atomic layer deposition process and thin layers for e.g. packaging purposes. The research partners included VTT, Advanced Surface Technology Research Laboratory at Lappeenranta University of Technology in Mikkeli, Finland and Department of Materials Science at Tampere University of Technology, Finland. These projects had a common steering group consisting of representatives from the research partners, Tekes, Bemis Valkeakoski, Innovia Films, Miktech, Saarioinen, StoraEnso and UPM Raflatac. We thank the steering group members for their interest and valuable support throughout the project.

The responsible director at VTT was Vice President Satu Helynen. The project managers at VTT were Terhi Hirvikorpi (1.8.2010-9.3.2011), Jenni Sievänen (10.3.2011-28.11.2012) and Mika Vähä-Nissi (29.11.2012-31.8.2013). The project core group at VTT included also Katri Behm, Emilia Kauppi, Hannu Mikkonen, Marja Pitkänen, Erkki Salo, Jari Vartiainen and Helena Wessman. We dedicate this report to Hannu Mikkonen who passed away during the project.

Finally, we want to express our gratitude to Prof. Maarit Karppinen, Leena-Sisko Johansson, Pia Sundberg and Anne Tanskanen from Aalto University, Timo Sajavaara from University of Jyväskylä, Khoren Sahagian from Anasys Instruments, Borealis Polymers and BI-AX International for their irreplaceable cooperation.

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1. Introduction

Atomic layer deposition (ALD) is a layer-by-layer process based on self-limiting gas-solid surface reactions [1-3]. Deposition cycles are repeated until the preferred layer thickness is obtained. ALD is suited for producing high-performance and dense inorganic films uniform in thickness. Most important commercial applications lies today in microelectronics, but they range from displays to protective coatings on silver jewelry. Future applications include packaging materials, devices for flexible electronics, membranes for environmental applications, and materials for energy applications. Continuous webs are of significant importance in several of these areas.

Barrier layers are required to decrease diffusion of, for example, water or oxygen. In the food packaging industry there is also a demand for light-weight and easy-to-recycle materials. On the other hand, barrier properties of biopolymers are not yet on a sufficient level for more demanding applications. ALD layers can lead to a dramatic improvement in the barrier properties.

However, adequate barrier properties are only one of the key requirements. Whenever a new packaging solution is developed product safety of the novel material should be confirmed. Dangerous products should never put on the market [4]. In addition to safety, sustainability issues should be taken into account in order not to create solutions that lead to loss of resources or acceleration of eutrophication or global warming via, for example, greater carbon foot print of the novel materials developed.

The base material affects thin film structure and properties. However, limited data is available concerning the effects of various polymer properties on nucleation, growth, resulting thin film structure and eventually on property improvement. In addition, only few processes can be applied for moving webs, which is a necessity for cost efficient large scale production. No industrial scale roll-to-roll process for ALD exists, although the basic characteristics required for such a process can be achieved.

2. Project goals

The role of VTT was to study technical feasibility of ALD with polymers using a batch reactor. Although the focus was on material research, this project also intended to alleviate the implementation of a roll-to-roll ALD process by creating the basis for optimizing the material and process parameters. The roll-to-roll processes will eventually enhance the techno-economic feasibility of ALD. The main goals were:

Studying polymer films and coated board as base substrates for ALD: Substrates to be studied included polymer films and biopolymer coated boards. The goal was also to prepare aqueous coatings with reduced moisture sensitivity to smooth the fiber webs, to test these on the pilot line and deliver them to the other tasks with essential information.

Understanding key parameters affecting thin layer growth and functional properties: Understand how the substrate properties and batch ALD process parameters affected nucleation, layer growth, and practical limitations as far as different material combinations were concerned. The purpose was to link the layer properties to the functional properties.

Characterizing of layers deposited by ALD, and production of thin layers: Understand the coating and the coating-polymer interactions applicable also to the roll-to-roll system, and the key functional properties of ALD layers particularly relating to thickness, cracking, etc. and their comparison with conventional ALD layers.

Assessing safety and sustainability: Estimate the safety aspects of material concepts utilizing ALD thin layers, perform LCA for the most potential materials, and to compare the performance of these to the competing solutions on the market for specific applications.

3. Materials

3.1 Precursors

The precursors for the Al_2O_3 depositions were water and ozone and trimethylaluminum (TMA; $Al(CH_3)_3$; SAFC Hitech, electronic grade purity), while ethylene glycol (min. purity of 99.5%, Riedel de-Haën) was used as the organic precursor in the hybrid alucone layers. High purity nitrogen gas was used as a carrier and purge gas. The precursors used for the ZnO depositions were diethylzinc (DEZ; SAFC Hitech, electronic grade, and Sigma Aldrich) and water/ozone. Ozone was created from oxygen with an ozone generator.

3.2 Films and coatings

Polymer films used during this project are listed below. Rayoface™ 50C, Evlon® EV 40 and OPET 23 films were three-layer structures: a core layer sandwiched between two thin skin layers. PLA was thermoplastic aliphatic polyester in this case supplied by NatureWorks™. Cellophane is antistatic and dimensionally stable. PLA has glass transition temperature of 60-65 °C, while for cellophane this is higher and undefined. Please contact the suppliers for further information about these polymer films.

- Two thickness of anchored uncoated cellophane films, Innovia Films,
- NatureFlex™ 42 NP (transparent 42 µm cellophane film), Innovia Films,
- NatureFlex™ 45 NVL (both side coated 45 µm cellophane film), Innovia Films,
- Rayoface™ 50C (biaxially oriented 50 µm polypropylene film), Innovia Films,
- BV301050 (50 µm polyhydroxybutyrate/polyhydroxyvalerate film), Goodfellow,
- Opalen 65 (laminate of 15 µm oriented polyamide and 50 µm polyethylene), Bemis,
- OPET 23 (biaxially oriented 12 µm polyethylene terephthalate film), Bemis,
- Evlon® EV 40 (biaxially oriented 40 µm polylactic acid film), Bi-Ax International,
- Polyethylene films, Borealis Polymers.

Coated paperboard samples included 210 g/m^2 Cupforma Classic from StoraEnso extrusion coated with 30 g/m^2 polylactic acid (PLA) and 30 g/m^2 low-density polyethylene (LDPE) at the extrusion coating pilot line at Tampere University of Technology. These samples were pre-treated prior to ALD at SutCo pilot coating line at VTT with corona and argon plasma.

An aqueous pectin/nanoclay mixture was coated onto 250 g/m^2 EnsoCoat from StoraEnso with the SutCo line. Other coatings listed below were coated onto 210 g/m^2 Cupforma Classic with a rod metering laboratory coater followed by drying in an oven at 105 °C. Some of the samples were also pressed in a hydraulic press or calendered to enhance film formation and surface smoothness.

- PEC (mixture of 5% pectin and 2% of nanoclay), VTT
- AP2 dispersions (modified starch acetate pigment as such and with plasticizers), VTT
- PLA dispersion (dispersion from Ingeo™ 3051D polymer from NatureWorks), VTT
- HLIG and SLIG dispersions (hardwood and softwood kraft lignin laurate), VTT

4. Methods

4.1 Deposition

Inorganic and hybrid layers were deposited on various polymer films and coated paperboards. These depositions were carried out in a commercial Picosun SUNALE™ ALD reactor in semi-clean test environment at VTT. Deposition temperature was 50-100 °C. Characteristic features of this reactor include:

- Inorganic and/or organic precursors
- Sources for liquid, solid or gaseous precursors
- Adjustable reactor temperature 50-500 °C
- Adjustable precursor source temperature (specific design low pressure precursors) NEW!
- Adjustable gas flows, and flow/no-flow NEW!
- Sample holder for single/multiple silicon wafers

During the project the reactor was updated to handle also solid precursors at elevated temperatures.

4.2 Structural and chemical characterization

Thin layer thickness on polymer films could not be measured directly, as poor thermal properties of polymers prevented the use of currently available analyzing tools. Therefore, the apparent thicknesses were determined for layers deposited in a separate run with the same process parameters on silicon wafers; thicknesses and refractive indices were then determined with a single wavelength ellipsometry (SE400adv, Sentech Instruments GmbH, angle of incidence of 70°) at VTT. Due to the different surface chemistries the actual growth rate on the polymers may, however, deviate from that on a silicon wafer. X-ray reflectivity (X'Pert Pro MPD, Panalytical, Cu Kα irradiation with wavelength of 1.5418 Å) was used to determine the densities of the thin layers. X-ray fluorescence (Axios mAX, 3 kW WDXRF Spectrometer, Panalytical) was tested at Aalto University for measuring thin layer thickness.

X-ray diffraction measurements were performed for selected samples to obtain information about the structure and orientation of crystallites within the thin layer (X'Pert Pro MPD Alpha1 from Panalytical using Cu Kα radiation with wavelength of 1.54056 Å). These measurements were performed at Aalto University.

Surface roughness R_a (µm) of polymer films was measured with a surface profilometer (Mitutoyo Formtracer SV-C3100) according to ISO 4288:1998. The load on the trailing tip was 4 mN. The result is an average of five scans in different directions.

Surface chemical composition was analyzed with X-ray photoelectron spectroscopy (XPS) at Aalto University using an AXIS 165 electron spectrometer, monochromatic Al Kα irradiation at 100 W, a slot-M lens configuration and a charge neutralizer. Fourier transform infra-red spectroscopy was used to investigate the chemical compositions of the ALD layers. Compositions of selected samples were also analyzed with time-of-flight elastic recoil detection analysis at University of Jyväskylä.

Scanning electron microscopy (SEM, LEO DSM, 982 Gemini FEG-SEM) was used to image the surfaces of the thin layers deposited onto polymer surfaces, while atomic force microscopy (AFM) was used to study the topography and the morphology of the polymer substrates before and after atomic layer deposition. AFM was carried out using a digital Nanoscope IIIa Multimode scanning probe microscope (Digital Instruments Inc.) in a tapping mode. Topographic AFM images were also assessed for surface roughness.

Contact angle and surface energy measurements (KSV CAM 200 Optical Contact Angle Meter) were carried out for the films in a controlled atmosphere (relative humidity 50%, temperature 23 ºC) with 10 parallel measurements for each test liquid. For the surface energy measurements water, di-iodomethane and formamide were used as the test liquids. The surface energies were calculated from the contact angle data by using the OWRK method and expressed as mN/m. This method utilizes a geometric mean equation for determination of the total surface energy and its polar and dispersive components of the solid surfaces. These components of the surface energy are determined by contact angle measurements of two or more liquids with known surface tension components.

Nano-thermal analysis (nanoTA) measurements were carried out with Anasys Instruments afm+i™. Localized thermal analysis was made using an AN2-200 µm Thermalever™ probe. Temperature was linearly ramped from ambient to a local softening temperature. Softening was defined by a specific downward deflection of the probe. Softening temperature (T_s) is related either to the glass transition or the melting temperature of the polymer being tested.

4.3 Functional characterization

Oxygen transmission rates (OTR) were determined with Systech M8001 and Mocon Oxtran 2/20 at 23 °C and either at 0 or 50 % relative humidity. Polymer films and polymer coated boards were clamped into the diffusion cell. The carrier gas was then routed to the sensor until a stable zero level was established. Pure O_2 was then introduced into the outside chamber of the diffusion cell. The flux of O_2 diffusing through the sample to the inside chamber was conveyed to the sensor. OTR was expressed as $cm^3/m^2/10^5$ Pa/day.

Water vapor transmission rate (WVTR) refers to the amount of water vapor transmitted through an area in certain time under specified conditions of temperature and humidity. The WVTR was measured by the gravimetric cup method where the substrate is sealed to the absorbent containing cell and exposed to humid air in a controlled environment. Test conditions were typically 23 °C and 50 % humidity. The values were expressed as g/m^2/day.

Mechanical properties were studied, for example, at Aalto University by straining samples in a mechanical tensile tester (MTS) having a load cell of 200 N and test velocity of 12 mm/min. Samples were stretched below the maximum elongation at break, i.e. typically a few %. Scanning electron microscopy was used to image the surface of the coatings deposited on polymer film before and after straining.

Thin layers were also evaluated with nanoindentation. The load placed on a hard tip was increased as it penetrated into the specimen soon reaching a user-defined value. A record of the depth of penetration was made, and the area of the indent was determined using the known geometry of the indentation tip. These values were then plotted on a graph to create a load-displacement curve. Hardness was defined as the load divided by the indentation area. Elastic modulus means the substance's tendency for elastic deformations.

Microscratch test was performed with a CSM Micro-Combi Tester. The idea was to scratch the sample surface with a loaded diamond tip. The system measured acoustic emission which indicated vibration of the tip due to a disturbed movement on the surface.

Polymer films with ALD layers were also tested against abrasive stresses. These tests were carried out using Taber Abraser with Calibrase® CS-10F disc for light abrasion and with a rubber disc without abrasive components. During Taber abrasion testing particle count was measured from air with ELPI (electric low pressure impactor), CPC (condensation particle counter) with the testing point 10 cm above the sample, and Hauke LPI (Hauke low pressure impactor) 50 cm above the sample. Also Wallace abraser was used. In this case abrasion was performed by abrasing the studied surface against itself.

Antimicrobial activity was evaluated with two methods. Antimicrobial activity was screened using agar diffusion assay according to EN 1104 (Hemmhof test) commonly applied to evaluate materials for food contact. The sample was placed on a semi solid nutrient medium in which an appropriate inoculum is mixed and then incubated. After incubation an existence of an inhibition zone (no germ growth or reduced growth) around the sample indicated antimicrobial activity. Test strains applied were a bacterium *Bacillus subtilis* TACC 6633 and a fungus *Aspergillus niger* TACC 6275. *Aspergillus niger* is a common food contaminant, while *Bacillus subtilis* is a gut bacteria in humans and a Gram-positive aerobic spore former. Exposure temperatures were 30 and 25 °C, and exposure times 72 and 120 h, respectively. Antimicrobial effect of the ALD thin layers was tested at VTT Expert Services Ltd.

The antimicrobial activity was also tested according to a Japanese standard JIS Z 2801. The samples and the non-antimicrobial reference material were cut to 5 cm x 5 cm pieces. 400 µl of bacterial solution was placed on each piece, and the solution was covered with a plastic film. Immediately after the inoculation the bacterial solution was washed from three reference samples and the amount of viable bacteria was determined by an agar culture method. The samples and the remaining references were incubated for 24 h at 35 °C. After the incubation the bacterial solution was washed from the samples and the amount of viable bacteria was determined by the agar culture method. The bacterial amounts were expressed as colony forming units on each test piece. Antimicrobial activity (R) was expressed as the difference in the logarithmic value of viable cell counts between the samples and the untreated products after inoculation and incubation of bacteria. This should be ≥ 2 for antimicrobial activity. The test bacterium was *Esherichia Coli* IFO 3972. E. Coli is a Gram-negative rod-shaped bacterium and present in human gut. The difference between the test procedures was that in the EN 1104 the reduction of germ growth around the sample, i.e. leaking of the antimicrobial constituents, in indirect contact is of interest, while in the JIS Z 2801 the reduction of germ growth on the test surface matters.

4.4 Safety and sustainability

Migration of aluminum from ALD layers to food simulants was studied with simulants used in testing of migration of substances from food contact materials. ALD coated polymer films were cut to 5 cm × 5 cm pieces. The food simulants were ethanol (10 %), acetic acid (3 %) and water at room temperature. Samples were placed in the simulant for 3 and 10 days. Volume of simulant per surface area of the sample was 100 ml/dm^2. Simulants without samples were used as references. Aluminum content in the simulant was analyzed using inductively coupled plasma-mass spectrometry (ICP-MS). Determination limit for ICP-MS was 0.5 µg/l corresponding to Al migration of 0.05 µg/dm^2. Al determinations were carried out in Labtium Oy.

Life cycle assessment (LCA) is a standardized method used for assessing the potential environmental impacts of a product or a service. The standards of LCA are ISO 14040 and 14044. The life cycle is modeled from unit processes connected to each other with material or energy flows. Each process has inputs and outputs connected to previous and following ones from the beginning until the end of the life cycle. “Cradle to grave” approach includes the production of raw materials and energy, manufacturing of the product, transportations, use phase, and disposal of the product or other end-of-life treatment. “Cradle to gate” and “cradle to customer” consider the life cycle until the production of the product or until the product has been transported to the customer.

LCA has four stages (Figure 1). Goal and scope defines the goal of the study, sets the boundaries and lists the assumptions needed. The life cycle inventory includes data collection and a balance calculation to all unit processes in the life cycle. The results are presented as inputs and outputs of the entire system. The results from the inventory can be converted into impacts in the third stage, the impact assessment such as carbon footprint calculation. The final stage of LCA is interpretation of the results based on all three previous stages. The results of LCA are represented per functional unit, which describes the need fulfilled with the product or service. Typical units are numbers or amounts of product.

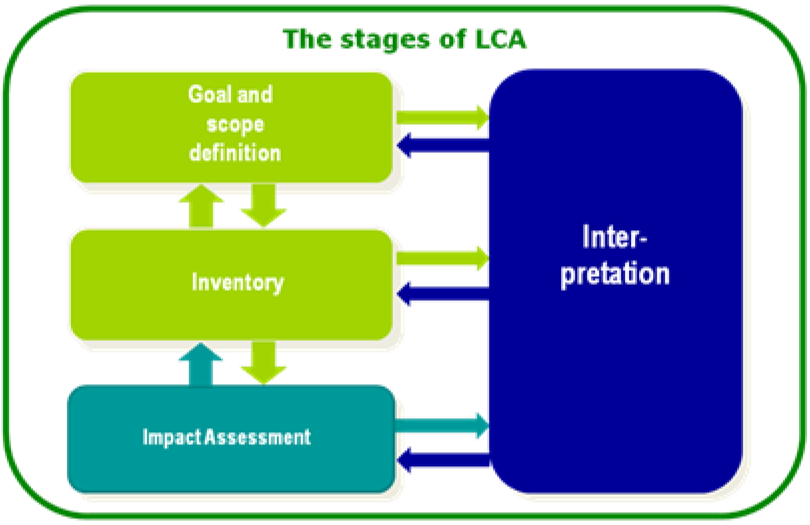

Figure 1. The four stages of life cycle assessment.

Carbon footprint describes the greenhouse gases released during the life cycle of a product. The most reliable way to study carbon footprint is to make an LCA calculation and consider only the greenhouse gases. Important greenhouse gases are fossil carbon dioxide (CO_2), methane (CH_4) and dinitrogenmonoxide (N_2O). Greenhouse gases are converted into carbon dioxide equivalents (CO_2 eq.) by multiplying them with factors given by Intergovernmental Panel on Climate Change. The total CO_2 equivalents are reported as carbon footprint.

5. Polymer films and coated board as base substrates (Task 3)

The purpose was to test different substrates including polymer films and biopolymer coated boards. The goal was also to prepare aqueous biopolymer coatings with reduced moisture sensitivity to smooth the fiber-based material. The idea was to take the best formulations to the pilot line and to characterize the samples to be used as the base substrate for the ALD. Examples of scientific articles and presentations in this area during the project are provided below. These contain details and additional results not necessarily included in this report.

- Vähä-Nissi, M., Hirvikorpi, T., Sievänen, J., Matilainen, K., Salo, E. and Harlin, A., “Atomic Layer Deposition of Thin Inorganic Coatings onto Renewable Packaging Materials”, Solid State Phenomena, 185 (2012) pp. 12-14.
- Vähä-Nissi, M., Salo, E., Sievänen, J., Pitkänen, M., Kenttä, E., Putkonen, M., Rättö, M. and Harlin, A., “Atomic layer deposited thin barrier films for packaging”, Submitted to PTS Symposium of Innovative Packaging 2014.
- Vähä-Nissi, M., Hirvikorpi, T., Sievänen, J., Matilainen, K., Salo, E. and Harlin, A., “Atomic Layer Deposition of Thin Inorganic Coatings onto Renewable Packaging Materials”, ICMAT International Conference on Materials for Advanced Technologies, Singapore, 2011.

5.1 Polymer films as substrates for ALD

Table 1 presents the effect of an ALD deposited 25 nm thick Al_2O_3 layer on the water vapor and oxygen barrier properties of various polymer films. Water and ozone were compared as the oxygen source. Deposition temperature was 100 °C and the deposition cycle 0.1/6/0.1/6 s for the $TMA/N_2/H_2O/N_2$ -process. Later we have prolonged the water pulse to 0.2 s.

Table 1. Oxygen and water vapor barriers of polymer films with 25 nm of ALD grown Al_2O_3.

Polymer	**OTR, RH 50% ($cm^3/m^2/10^5$ Pa/day)**		**WVTR, RH 50 %, ($g/m^2/d$)**	
	water	**ozone**	**water**	**ozone**
Anchored cellophane	> 400	> 400	290	290
+ 25 nm ALD Al_2O_3	4.9	9.5	< 1.0	11
NatureFlex™ 42 NP	16	16	100	100
+ 25 nm ALD Al_2O_3	8.9	< 0.1	44	18
NatureFlex™ 45 NVL	12	12	35	35
+ 25 nm ALD Al_2O_3	5.6	< 0.1	2	2.4
Rayoface™ 50C	1300	1300	< 1.0	< 1.0
+ 25 nm ALD Al_2O_3	4.5	6.2	< 1.0	< 1.0
BV301050	> 400	> 400	8.3	8.3
+ 25 nm ALD Al_2O_3	2.1	< 0.1	1.0	-
Opalen 65	53	53	< 1.0	< 1.0
+ 25 nm ALD Al_2O_3	10	0.2	< 1.0	< 1.0
OPET 23	68	68	3.1	3.1
+ 25 nm ALD Al_2O_3	2.3	< 0.1	< 1.0	< 1.0
Evlon® EV 40	> 400	> 400	21	21
+ 25 nm ALD Al_2O_3	4.5	< 0.1	< 1.0	< 1.0

The best oxygen barriers with the Al_2O_3 thin layer were PHB/HV (BV301050) and OPET films, and the best water vapor barriers BOPP (Rayoface™ 50C), Opalen 65, OPET and BOPLA (Evlon® EV 40) films. However, the most significant overall improvements in barrier values were observed with the anchored cellophane, BOPLA, PHB/HV and OPET films. This indicated that proper surface chemistry, and oxygen containing groups in specific, enhances thin layer uniformity. Cellophane is rich in hydroxyl groups, while the three polyesters have similar -(C=O)-O- groups in the main molecule chain available for reactions with the precursors. These are sites for chain scission and formation of further functional groups.

Table 2. Surface energy (mN/m), relative polarity (%) and roughness (R_a; μm) of films.

Polymer	**Surface energy (mN/m)**			**Polarity (%)**	**R_a (μm)**
	dispersive	**polar**	**total**		
Anchored cellophane	34.6	13.4	48.0	33.5	0.07
NatureFlex™ 42 NP	33.6	36.3	69.9	52.0	0.06
NatureFlex™ 45 NVL	33.7	5.0	38.7	12.9	0.03
Rayoface™ 50C	31.5	5.3	36.9	14.4	0.03
BV301050	33.8	10.1	43.9	23.0	0.12
Opalen 65	35.5	4.9	40.4	12.1	0.05
OPET 23	39.9	9.8	49.6	19.8	0.03
Evlon® EV 40	34.9	11.1	46.0	24.1	0.04

Replacing water with ozone as the oxygen source improved in most cases the oxygen barrier of the polymer films. This was less obvious or even the opposite for the water vapor barrier due to a different diffusion mechanism and more uniform but also more polar oxide layer.

Polymer films were also characterized for surface energy and surface roughness (Table 2). There were no clear correlation between these parameters and the barrier properties after the ALD deposition, although the films with the most enhanced barrier properties also had a high relative polarity. Contact angles are often more feasible for larger surface features. In addition, the initial reactions between the precursors and the polymer could well change the surface chemistry as pointed out elsewhere in this report.

During the project only one polymer film turned out to be problematic; a polyethylene film with an antioxidant agent totally prevented the growth of Al_2O_3 with the TMA-water process without surface activation with ozone as presented in Chapter 6.2. However, results with the corona-treated BOPP film (Rayoface™ 50C) and LDPE film without the antioxidant indicated that Al_2O_3 can also be deposited onto polyolefin films with the ALD.

5.2 Coated boards as substrates for ALD

PLA and AP2 starch dispersions with and without plasticizers had poor barrier properties. PLA dispersion (~ 10 g/m^2), for example, provided a grainy surface, which indicated poor film formation even after hot compaction. The surface of plasticized AP2 starch coating was smooth and glossy after hot compaction, and the gas barrier was moderate (OTR ~5000 $cm^3/m^2/10^5$ Pa/day). However, the coating was transferred easily to the hot surfaces, which eventually ruined the coating. The coating weight of starch coatings was 10-25 g/m^2. ALD reactor temperature was 100 °C and deposition was performed with TMA and water.

Lignin laurate dispersions (HLIG and SLIG) did not form very good oxygen barriers, and although oxygen barrier was significantly improved by 25 nm of Al_2O_3 the values were not good enough for several packaging applications (Table 3). This was probably due to the poor uniformity of the lignin coatings.

Table 3. Effect of 25 nm Al_2O_3 on the oxygen barrier of lignin laurate coated board.

Lignin derivative	**Coat weight (g/m^2)**	**OTR, RH 50% ($cm^3/m^2/10^5$ Pa/d)**	
			+ 25 nm ALD Al_2O_3
Soft wood kraft lignin laurate	11	58000	3000
Soft wood kraft lignin laurate	15	36000	1700
Hard wood kraft lignin laurate	10	55000	2200
Hard wood kraft lignin laurate	15	37000	3200

Pectin/nanoclay mixture proved to be a potential alternative (Table 4). The coating weight was adjusted with multiple coating runs. In addition, the base substrate was pigment coated. Therefore, it is likely that part of the positive effect of the ALD deposited Al_2O_3 was due to the enhanced uniformity and smoothness of the PEC coating with increasing coating weight.

Table 4. Effect of 25 nm Al_2O_3 on the barrier properties of pectin/nanoclay coated board.

PEC (g/m^2)	**OTR, RH 50% ($cm^3/m^2/10^5$ Pa/day)**		**WVTR, RH 50 %, ($g/m^2/d$)**	
		+ 25 nm ALD Al_2O_3		+ 25 nm ALD Al_2O_3
6.8	9130	1850	87 ± 9	3.1
9.2	265	2.5	96 ± 7	< 1.0
15	1	< 0.1	67 ± 5	< 1.0

6. Key parameters for thin layers & functional properties (Tasks 4)

The main goal was to understand how the substrate properties and batch ALD process parameters affect nucleation, layer growth, and practical limitations as far as different material combinations are concerned. Further on, the purpose was to link the layer properties to the functional properties and to obtain detailed understanding of the coating and the coating-polymer interactions. The main scientific articles and presentations in this area are listed below. These contain details and additional results not necessarily presented in this summary report.

- Vähä-Nissi, M., Pitkänen, M., Salo, E., Tanskanen, A., Sajavaara, T., Putkonen, M., Sievänen, J., Kenttä, E., Rättö, M., Karppinen, M. and Harlin, A., "Antibacterial and barrier properties of oriented polymer films with ZnO thin film applied with atomic layer deposition at low temperatures", To be resubmitted to Thin Solid Films, 2013.
- Vähä-Nissi, M., Kauppi, E., Sahagian, K., Johansson, L.-S., Peresin, M.S., Sievänen, J. and Harlin, A., "Growth of thin Al_2O_3 films on biaxially oriented polymer films by atomic layer deposition", Thin Solid Films, Vol. 522 (2012) pp. 50-57.
- Vähä-Nissi, M., Sundberg, P., Kauppi, E., Hirvikorpi, T., Sievänen, J., Sood, A., Karppinen, M. and Harlin, A., "Barrier properties of Al_2O_3 and alucone coatings and nanolaminates on flexible biopolymer films", Thin Solid Films, Vol. 520 (2012) pp. 6780-6785.
- Kauppi, E., "Alucone and alumina thin films on biopolymers deposited by Atomic Layer Deposition (ALD) and Atomic layer deposition/Molecular layer deposition techniques (ALD/MLD", Master's thesis, School of Chemical Technology, Aalto University, 2011.
- Vähä-Nissi, M., Sievänen, J., Salo, E., Pitkänen, M. and Harlin, A., "Thin Al_2O_3 barriers on polymer films", International Workshop, Action COST FA0904, Prague, Czech Republic, 2013.
- Vähä-Nissi, M., "Atomic layer deposited thin-layers for upgrading bio-based materials", in Research highlights in industrial biomaterials (Sundqvist, H., Ed.), VTT, 2012, pp. 63-68.
- Vähä-Nissi, M., Hirvikorpi, T., Sievänen, J., Salo, E., Harlin, A., Johansson, P. and Kuusipalo, J., "Effect of pre-treatments on barrier properties of layers applied by atomic layer deposition onto polymer-coated substrates", 13th European PLACE Conference 2011, Bregenz, Austria.

6.1 Growth of Al_2O_3 layer on polymers

Changes on polymer film surfaces during the Al_2O_3 growth at low deposition temperatures were followed. Initially, precursor is sorbed onto and into the polymer [5-7]. Different gas-solid reactions are possible [8]. In the absence of reactive polymer groups the non-desorbed TMA is available for subsequent reaction with water, and water and reaction by-products can create additional reaction sites. These reactions form the basis for nucleation and initial layer growth. BOPLA film had a higher number of polar groups, such as carbonyls and hydroxyls, suitable for chemical interactions than BOPP film. In spite of a smoother surface, more aluminum was therefore deposited on BOPLA leading to better coverage. The decrease in the relative number of carbon-oxygen groups in BOPLA indicated chemical interactions with TMA. As demonstrated in Chapter 5.1, processing additives such as antioxidants can also prevent layer growth completely.

Figure 2 shows the ALD growth mechanisms on polymer surfaces. During the initial growth metal oxides started forming clusters [5,9,10]. Layer growth continued through clusters, and this was more pronounced with the hydrophobic BOPP. These clusters can affect the surface topography even after the surface is covered with Al_2O_3. Softening temperature (T_s) of both polymer surfaces increased with the number of deposition cycles, mainly due to the increased thickness of the Al_2O_3 layer. However, with BOPLA the initial deposition cycles decreased deviation in T_s due to a near surface interphase formed as a result of the chemical interactions discussed above. A further increase in the ALD cycles increased T_s, but more irregularly, indicating cluster growth. With BOPP the relative increase in T_s was more moderate. Resolution was not high enough to detect clusters, which explained a more or less constant standard deviation for T_s.

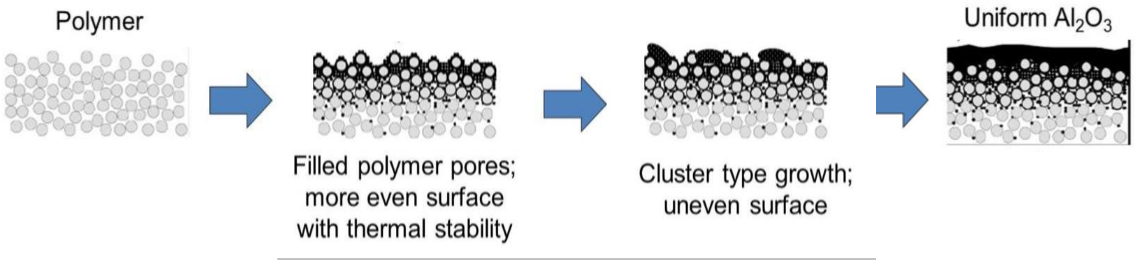

Figure 2. Growth of inorganic ALD layers on non-ideal polymer substrates.

6.2 Process optimization

Surface chemistry of polymer films has an impact on thin layer growth as indicated by corona and argon plasma pre-treatments for LDPE and PLA coated (30 g/m^2) boards prior to the ALD. Corona and plasma are commonly used in various industrial applications such as paper and film converting to adjust surface polarity and wetting characteristics. The target treatment level at the SutCo pilot line was 50 Wmin/m^2. ALD deposition was performed with TMA and water immediately after the pre-treatment at 80 ºC to avoid aging and surface contamination.

Both pre-treatments improved the barrier properties (Figure 3). It was also assumed that the effect would be more profound with thinner (12.5 nm) Al_2O_3 layers, which proved to be true. Thin layers are more sensitive for the early layer growth and layer uniformity. However, the barrier properties with thicker (25 nm) Al_2O_3 layers were also improved, albeit the relative improvement was not as significant. Corona treatment has several beneficial effects the most significant of which is the formation of oxidized groups [11]. Argon plasma does not add new chemical functionalities to the surface, but creates radicals reacting later with oxygen in the air. This could explain why corona was slightly better than Argon plasma.

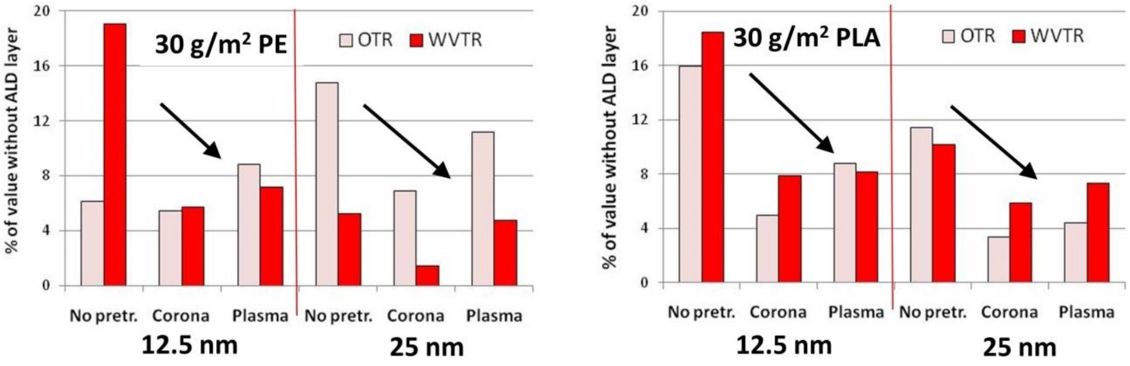

Figure 3. Relative improvements in water vapor and oxygen barriers by corona and argon plasma pre-treatment of LDPE (left) and PLA (right) -coated boards prior to ALD deposition of Al_2O_3 with TMA and water at 80 ºC.

Both pre-treatment methods are commercially available for web materials. However, it is important to install these units so that the oxidizing is maximized but the film would have neither time nor possibility to attract particulate contaminants before thin layer deposition.

ALD depositions were performed at different process conditions. The parameters included reactor and precursor temperatures, precursor pulsing times, purging time and amount of different gases in the carrier flow. Reactor and precursor temperatures are important parameters affecting thin layer growth and structure. Reactor temperature was between 50-100 ºC. ALD layers deposited at low reactor temperature contain typically more hydrocarbon impurities than layers deposited at higher temperatures. These impurities together with lower layer density may impair barrier properties, although in the case of ZnO it was layer uniformity rather than high density that mattered. Reactor temperature should be as high as possible and yet lower than the temperature at which the polymer degrades, melts or softens. This is equally important for both the batch and the roll-to-roll ALD process.

Precursor pulsing times should be long enough to deliver enough precursors to complete monolayer growth rate. Purging should be efficient enough to remove the non-reacted precursors and the reaction by-products. These parameters are reactor type and design dependent and cannot be treated as de facto in every process and are therefore secondary in understanding how substrate properties and ALD process parameters affect layer growth. However, ALD at low temperatures requires often longer exposure and purge times and thus increased overall cycle times. For example, purging of H_2O takes longer at low temperatures because of slower desorption of H_2O from reactor walls.

Oxidizing agent in ALD is typically water. Replacing water with ozone improved the barrier properties in general and oxygen barrier in specific. In addition, ozone does not leave hydrogen impurities in the deposited Al_2O_3 layer. The growth rate with ozone was usually similar or lower than with water. Somewhat better oxygen barrier properties have been achieved also earlier with a TMA-ozone process compared to TMA-water [12]. This is less obvious or the opposite for the water vapor barrier due to a different diffusion mechanism and more uniform but also more polar oxide layer. Also diethylzinc (DEZ) provided better oxygen barrier with ozone than with water at deposition temperature of 100 ºC. Unlike TMA, DEZ is more sensitive to the reactor temperature. In addition, reactions seem to be more complicated between DEZ and ozone than with water leading to the formation of zinc salts of carboxylic acids at low temperatures. Use of ozone resulted also in lower layer density. Figure 4 shows results covering both oxygen sources and pre-treatments.

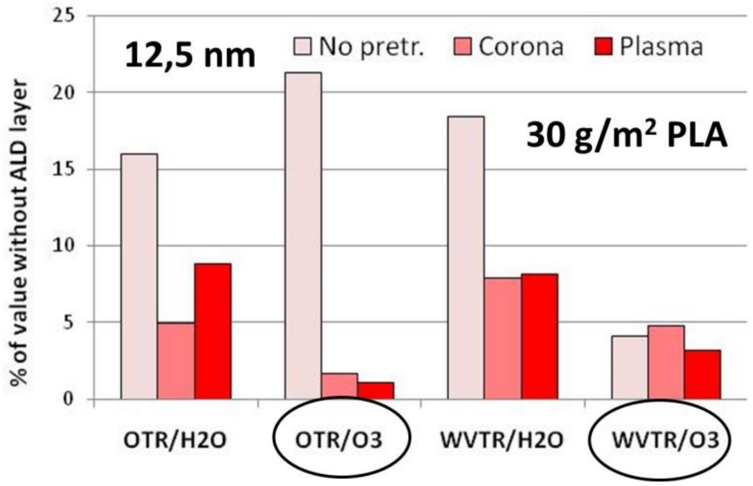

Figure 4. Effect of oxygen source (water vs. ozone) and pre-treatment on the oxygen and water vapor barrier properties of PLA coated paperboard with 12.5 nm of Al_2O_3.

The strong oxidizing power of ozone can be used to modify polymers not otherwise feasible for the ALD. Figure 5 shows an example of a polyethylene film containing antioxidant as an additive. This blocked completely nucleation and layer growth with the TMA-water process at 100 ºC. However, after 20 pulses of ozone to the reactor Al_2O_3 layers could be grown successfully also with the water process. TMA-ozone process did not need such a pre-treatment for film growth. A similar effect has also been observed with an untreated BOPP film.

With the exception of the most sensitive polymers which might not withstand the oxidizing power of ozone, the ozone process is a highly potential alternative for depositing Al_2O_3 and ZnO onto biopolymers. Replacing water in the roll-to-roll ALD process requires only investments in oxygen gas, an ozone generator and certain occupational safety measures.

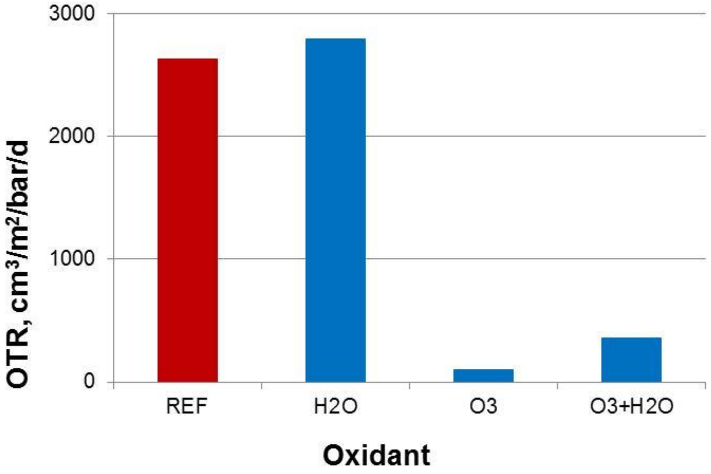

Figure 5. Comparison of Al_2O_3 layers deposited with TMA-water, TMA-ozone and 20 pulses of ozone followed by TMA-water processes onto LDPE film with an antioxidant additive.

Another option is to promote absorption of TMA into the polymer film during the first ALD cycles. This was tested by increasing the duration of the first TMA pulse and then continuing with 99 normal deposition cycles. We assumed that enhanced absorption of precursor into the polymer and formation of a interphase could lead to a somewhat improved water vapor barrier. However, absorption improved also the oxygen barrier by 20-30 %, especially with more polar BOPLA film (Figure 6). However, the overall layer thickness might have also increased. Changing length of a single precursor pulse in the current roll-to-roll ALD setup can be difficult if not impossible.

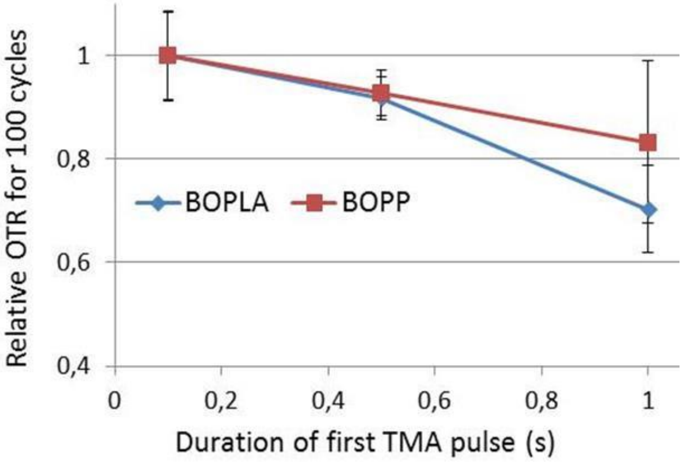

Figure 6. Effect of the first TMA pulse length on the oxygen transmission rate ($cm^3/m^2/10^5$ Pa/day) through BOPP and BOPLA films after 99 deposition cycles with 0.1 s TMA pulses.

6.3 Mechanical properties of ALD layers

Flexibility is a key requirement for several packaging materials. These materials are exposed to various mechanical stresses during converting and packaging processes. Inorganic coatings have often poor mechanical properties, which results in film cracking and impaired barrier properties [13–16].

Abrasion resistance of BOPLA and anchored cellophane with 25 nm of Al_2O_3 was evaluated. Both Taber and Wallace tests were used. In Taber test the rubber roll without extra loading was used. While the deposition of Al_2O_3 onto cellophane was performed only at 80 ºC, the deposition temperatures were 50, 80 and 100 ºC for BOPLA.

Table 5. Oxygen transmission rates ($cm^3/m^2/10^5$ Pa/day) of BOPLA and cellophane films with 25 nm Al_2O_3 after abrasive testing. OTRs of uncoated films exceed 400 $cm^3/m^2/10^5$ Pa/day.

Material	**Before abrasion**	**Taber abraser; rubber disc**	**Wallace abraser Al_2O_3 with Al_2O_3**	
		100 cycles	20 cycles	50 cycles
BOPLA, 50 ºC	1.3	148		260
BOPLA, 80 ºC	1.1	123	190	210
BOPLA, 100 ºC	1	91	96	126
Anchored cellophane	0.1	0.1	6	5

Both tests had a dramatic effect on the polymer films. However, the relative increase in oxygen barrier was larger with BOPLA (Table 5). We attribute this to the different polymer surface chemistries, which affected the layer growth and the final layer properties. The results also indicated that a higher deposition temperature is favorable. Figure 7 shows examples of cellophane film after the Wallace test. It is obvious that a thin oxide layer has to be protected from abrasive stresses with an additional polymer layer.

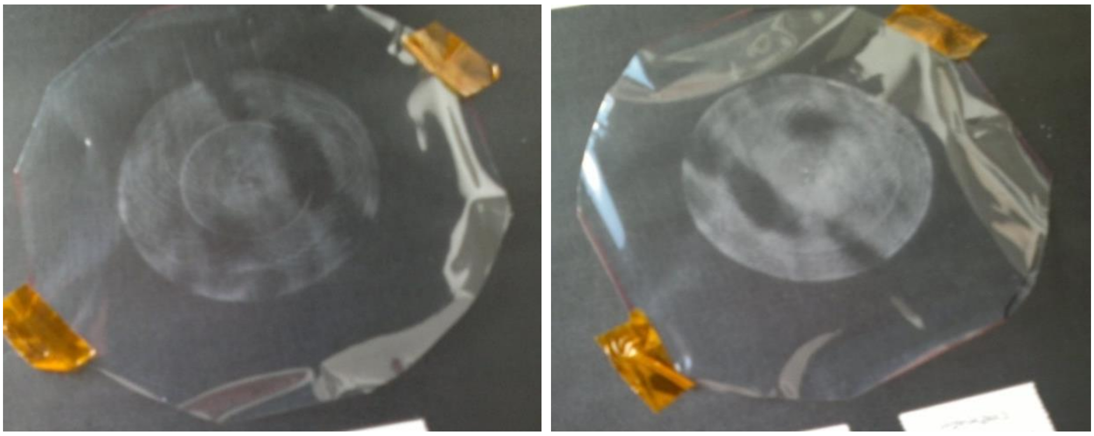

Figure 7. Cellophane with 25 nm Al_2O_3 after 20 (left) and 50 (right) cycles in Wallace abraser.

Flexibility of Al_2O_3 layers was improved by combining atomic and molecular layer deposition (MLD) techniques to create five-layer nanolaminates based on alternating layers of Al_2O_3 and inorganic–organic aluminum alkoxide (alucone). The flexibility of the polymer films with the thin layers was evaluated by uniaxial straining followed by barrier analyses and SEM imaging. Feasibility of combining weak layers was based on the idea that cracking does not take place in all the layers at the same point due to a more complex stress distribution.

The barrier properties of Al_2O_3 layers were deteriorated to a somewhat lesser extent when the layer thickness decreased. Al_2O_3/alucone –nanolaminates showed improved flexibility compared to Al_2O_3 layers (Figure 8). Not surprisingly, the laminates having the highest total thickness of Al_2O_3 provided the best overall barriers before straining. Flexibility of nanolaminates increased when the thickness of the individual Al_2O_3 layers decreased and alucone was used as a spacer between the Al_2O_3 layers. WVTR depended more on the overall film properties, such as layer thickness and chemistry. Also in this test straining impaired oxygen barrier more in the case of BOPLA, which we believe to be due to the different polymer surface chemistries and thus different thin layer growth dynamics.

Nanoindentation tests on different thin layers and nanolaminates deposited on silicon wafer indicated that the inorganic-organic hybrid also decreased the thin layer hardness and improved the elasticity out-of-plane (Figure 9). Microscratch test turned out not to be feasible for such thin layers and nanolaminates.

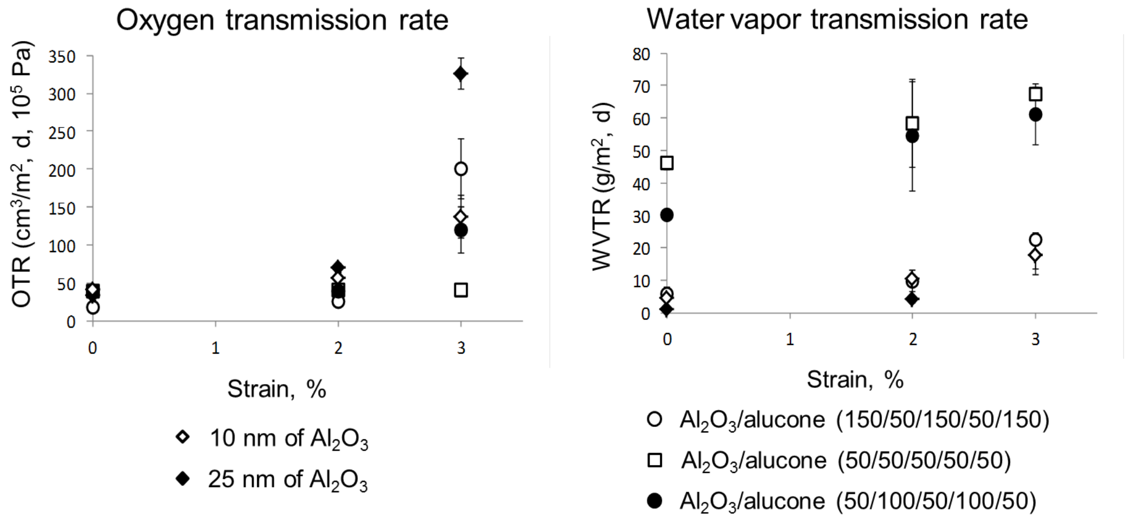

Figure 8. Effect of straining on oxygen (left) and water vapor (right) barriers of BOPLA film with Al_2O_3 layer and five-layer nanolaminates of Al_2O_3/alucone/Al_2O_3/alucone/Al_2O_3 –type.

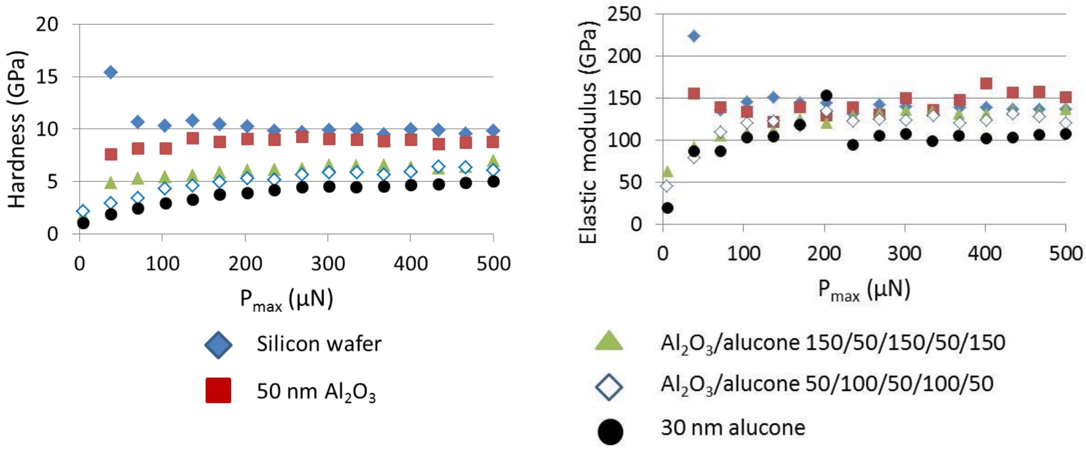

Figure 9. Hardness (left) and elastic modulus (right) of 50 nm Al_2O_3, 30 nm alucone and five-layer nanolaminates determined with nanoindentation.

Depositing nanolaminates with the current R2R ALD setup is not possible. However, poor flexibility and surface strength of inorganic thin layers is a drawback for many applications. Only nanolaminates based on one inorganic-organic hybrid were presented as means to improve flexibility – alternative solutions could include laminates with enhanced barrier also against moisture. In addition, thin layers have to be laminated between two polymeric substrates to protect them from mechanical stresses and to provide moisture barrier.

6.4 Antimicrobial thin barrier films

Concerns on food safety and quality, and need for extended shelf-life of packaged foods have promoted the development of antibacterial materials. Zinc oxide, for example, has been used in packaging applications and it can be added to food. ZnO has been tested as an antibacterial additive in polymer composites and in coatings [17-22] and membranes [23,24].

However, few studies were available covering antimicrobial and/or barrier properties of ZnO deposited with ALD at low temperatures on polymer films intended for packaging purposes. Diethylzinc (DEZ) used to grow ZnO has a high vapor pressure at room temperature and reactivity with water [25-27]. This makes ALD ZnO attractive for heat-sensitive polymers. ZnO is also inexpensive, stable and has interesting optical and electrical properties [28].

ZnO can be deposited onto oriented polymer films at temperatures ≤ 100 °C using ozone as the oxygen source instead of water. Growth rate was higher with water than with ozone. Ozone at 100 ºC provided the lowest ZnO growth rate but the best barriers relatively close to those obtained with Al_2O_3 of similar 25 nm thickness (Figure 10). The positive effect of ozone on the barrier properties at 100 °C was clear, although these layers had lower density and they contained zinc salts of carboxylic acids due to more complex chemical reactions between DEZ and ozone. A low growth rate promoted formation of uniform thin layers, while polar grain boundaries impaired the barrier properties of layers grown with water. The OTR is also generally regarded as more sensitive towards coating defects than the WVTR.

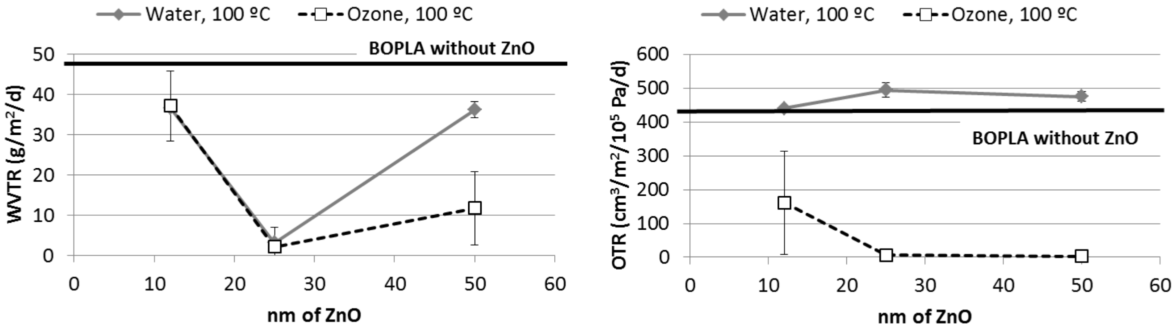

Figure 10. Example of barrier properties with ZnO thin layers; Water vapor (left) and oxygen (right) barriers of BOPLA with 25 nm of ZnO deposited with water and ozone at 100 °C.

Table 6. Effect of ZnO and Al_2O_3 deposited on BOPLA on the growth of Aspergillus niger and Bacillus subtilis. Inhibition zones over 0.5 mm can be detected.

Sample	**Aspergillus niger**	**Bacillus subtilis**
12.5 nm TMA / H_2O 70 °C	No inhibition zones	No inhibition zones
25 nm TMA / H_2O 70 °C	No inhibition zones	No inhibition zones
12.5 nm DEZ / H_2O 70 °C	No inhibition zones	No inhibition zones
25 nm DEZ / H_2O 70 °C	No inhibition zones	No inhibition zones
35 nm DEZ / H_2O 70 °C	No inhibition zones	No inhibition zones
50 nm DEZ / H_2O 70 °C	Inhibition zones (2-5 mm), detected in 19/20 pieces	Inhibition zones (2-8 mm) detected in all pieces
12.5 nm DEZ / H_2O 70 °C + UV	No inhibition zones	No inhibition zones
50 nm DEZ / H_2O 70 °C + UV	No inhibition zone. However, 6/20 test pieces showed growth reduction[a]	Inhibition zones (5 mm) detected in 12/20 test pieces
12.5 nm DEZ / H_2O 100 °C	No inhibition zones	No inhibition zones
50 nm DEZ / H_2O 100 °C	No inhibition zones	No inhibition zones
Reference, uncoated film	No inhibition zones	No inhibition zones

[a] According to EN 1104 evidence of an inhibition zone is given if there is no growth or a perceptible reduction of growth (approx. 20% less) than in the surrounding area.

50 nm of ZnO deposited with water at 70 ºC indicated migration of antibacterial agent (Table 6). However, a direct contact between both ZnO and Al_2O_3 layers and bacteria promoted antibacterial activity further (Table 7). This is likely due to more efficient migration through polar grain boundaries or from an amorphous layer in the latter test method. It is noteworthy that a nanolaminate consisting of 50 nm ZnO covered with a thin layer of Al_2O_3 retained most of its antimicrobial activity compared to plain ZnO.

Table 7. Antimicrobial activities calculated according to JIS Z 2801 for BOPLA with ALD deposited ZnO, Al_2O_3 and ZnO/Al_2O_3 nanolaminates. All samples were antimicrobial (R > 2).

Sample	**Antimicrobial activity R**
25 nm TMA / H_2O 70 °C	3.5
25 nm DEZ / H_2O 70 °C	5.9
50 nm DEZ / H_2O 70 °C	5.8
75 nm DEZ / H2O 70 °C	5.8
50 nm DEZ / H_2O 70 °C + UV	5.8
50 nm DEZ / H_2O 70 °C + 5 nm TMA / H_2O 70 °C	5.9
50 nm DEZ / H_2O 70 °C + 15 nm TMA / H_2O 70 °C	4.6
25 nm DEZ / H_2O 100 °C	2.3
50 nm DEZ / O_3 70 °C	5.8
50 nm DEZ / O_3 100 °C	5.8

As far as the roll-to-roll ALD setup is concerned a special construction or two separate units are required in order to be able to produce nanolaminates. A compromise regarding the deposition conditions or the nanolaminate structure might be necessary to meet both good barrier and antimicrobial properties. In addition, further tests, e.g. for migration and antimicrobial activity against other test strains, are required when estimating the full potential and performance of such thin layers and nanolaminates.

7. Safety and environmental hotspots of ALD coated films (Task 7)

This task had two goals. The first one was to estimate the safety aspects of specific material concepts utilizing the ALD layers developed during the project. The other one was to perform LCA for the same materials, and to compare the performance of these to the existing solutions for specific applications. This was later refocused to locate the environmental hotspots based on the LCA and carbon footprint data of materials used in packaging. The main articles and presentations provided in this area during the project are listed below. These contain details and additional results not presented in this report.

- Vähä-Nissi, M., Pitkänen, M., Putkonen, M., Sievänen, J., Salo, E. and Harlin, A., “Safety aspects of polymer films with thin Al_2O_3 thin barrier”, Coating International, 46 (2013) pp. 48-51.
- Vähä-Nissi, M., Sievänen, J., Pitkänen, M., Salo, E., Vartiainen, J. and Harlin, A., “Safety aspects of polymer films with atomic layer deposited Al_2O_3 thin layers”, TAPPI 14th European PLACE Conference proceedings, Dresden, Germany, 2013.
- Vähä-Nissi, M., Pitkänen, M., Salo, E., Sievänen, J., Putkonen, M. and Harlin, A., “Safety aspects of polymer films with atomic layer deposited thin Al_2O_3 barrier layers”, 13th International Conference on Atomic Layer Deposition, San Diego, USA, 2013.

7.1 Compliance of materials for food contact

Feasibility of the ALD coated polymer films developed in the project for food contact was assessed based on regulations and recommendations in EU and U.S. Current regulations reflect only the existing packaging solutions and materials. Therefore they might not be totally suitable for new materials and technologies. For example, it may be necessary to use substances that have not been applied in food contact materials (FCM). However, neither a procedure to obtain an authorization nor a complete test procedure needed to prove the suitability of a new material for food contact were included as this would have been too early.

In Europe food contact materials are regulated with *Framework Regulation* (EC No 1935/2004) [29] and with regulation on good manufacturing practice (EC No 2023/2006) [30], known as the *GMP Regulation*. These cover all materials and articles intended to come into contact with food, or can reasonably be expected to be brought into contact with food. Material combinations should also fulfill these regulations. The *Framework Regulation* states that food contact materials should be manufactured so that, under normal or foreseeable conditions of use the migration from the material to food is so slight that it could not endanger human health or change the key characteristics of packaged food. However, *Framework Regulation* doesn't give detailed guidelines how to demonstrate the safety.

Instead, the *GMP Regulation* gives more detailed rules on good manufacturing practice. It aims to ensure that finished materials and articles are produced in accordance with pre-established and well documented instructions, and thus comply with their specifications. According to the *GMP Regulation* all producers should have an effective quality management of their processes and it shall be applied to all sectors and stages of manufacturing, processing, and distributing food contact materials. The *GMP Regulation* specifies also general demands for quality assurance and control systems, and documentation related on them for all business operators in the supply chain.

Specific regulations are in place for plastic food contact materials [31], recycled plastics [32], regenerated cellulose film [33], ceramics [34], and active and intelligent materials [35]. All others, e.g. paper and board, are covered only by the general safety requirements set out in the *Framework Regulation* and a general obligation on good manufacturing practice.

For plastic food contact materials the Regulation EU No 10/2011 on plastic materials and articles intended to come into contact with food (*Plastics Regulation*) should be followed. The regulation applies to materials and articles consisting solely of plastics as well as to plastic multi-layer materials that consists several plastic layers. Both of the materials may be also covered by a coating, as is the case with ALD coated materials. Because specific measures can be adopted for the coatings under the EU legislation, but not yet legislated, the coatings are allowed to contain also other substances than those authorized at EU level for plastics. Such layers may be subjected to other EU or national rules, e.g. BfR recommendations or alike. Coatings are not yet subject to the requirement of a declaration of compliance. However, adequate information should be provided to the manufacturer of the packaging material or package to ensure compliance for substances to which migration limits are given.

The *Plastics Regulation* contains a list of substances authorized to be used in manufacturing of plastic materials and articles. Specific migration limits (SML) or maximum contents in plastic material (QM) are set for certain substances. A generic migration limit of 60 mg/kg food should be applied for substances for which no specific migration limit or other restriction is provided. In addition, plastic materials should not transfer their constituents to food in quantities exceeding 10 mg/dm^2 of food contact surface. The regulation defines food simulants and migration tests to be applied when suitability for food contact is assessed. Plastic materials may contain impurities originating from the manufacturing process not intended to remain in the food contact material. Therefore, they are not considered to be subject for the authorization process at EU level. However, if there is any potential health risk their use should be assessed by the manufacturer.

Migration of substance not listed in the Union list (non-authorized substances) should not exceed 0.01 mg/kg food. The substance should not be classified ‘mutagenic’, ‘carcinogenic’ or ‘toxic to reproduction’ (CRM) or be in nanoform. Nanomaterial is defined as *“a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm”* [36]. Substances in nanoform are allowed for food contact only when explicitly authorized.

In EU active and intelligent materials intended to come into contact with food are regulated with Regulation EC No 450/2009 [35]. Active materials actively affect the packaged food or its self-life. The chemical substances responsible for activity are either directly incorporated in the material or placed in separate container. Intelligent materials are defined as “materials which monitor the condition of the packaged food or the environment surrounding the food”, e.g. different indicators. Only authorized substances can be used. The first list is expected to be available towards the end of 2014 [37]. Substances that fully comply with relevant food legislation or are separated from food or its surrounding by a functional barrier are an exception. The substrate/passive part of the food package, e.g. packaging material itself, should be in accordance with corresponding EU or national requirements.

Based on our analyses uniform ALD Al_2O_3 barrier layers chemically bonded to the polymer films do not fall under the European Commission’s definition of nanomaterial. Therefore, ALD coating on polymer film or coated board should not be considered as nanomaterial although the thickness of the ALD grown layer is in the nanoscale. Instead, ALD layers resemble the metallized layers used in food packages for tens of years. Generally in the industry, the term “nanocoating” refers to coatings with thickness in the nm-range, e.g. vacuum metallization and inorganic oxide coatings. In addition, EFSA has given an opinion on a barrier nanocoating of SiO_2 formed on PET articles. According to EFSA testing of overall migration was not required due to very low thickness of the coating [38]. In addition, nanosilica is one of the nanomaterials accepted for plastic FCM.

Our opinion is that ALD coated film should be considered as a plastic covered by an inorganic coating. The polymer film should fulfill the requirements in the Regulation EU No 10/2011 on plastics. Today coatings are not covered by EU legislation and thus they may also contain substances not mentioned in the Plastics Regulation. However, ALD coated polymer film should fulfill the requirements given in the Framework Regulation and should be manufactured in accordance with the GMP Regulation. In addition, general safety requirements, such as specific migration limits of chemical substances, limits for non-intentionally added substances, etc., can be utilized.

7.2 Assessment of raw materials for food contact

Suitability of polymer films for food contact was evaluated based on the statement given by the manufacturers. Examples of food contact status of two oriented films used in this project are summarized in Table 8: BOPLA obtained from BI-AX International Inc. and top side corona treated BOPP from Innovia Films. In addition to regulations and recommendations, information about the food contact, for example food type and intended conditions of use, is needed when planning the testing strategy for the ALD coated polymer films.

Suitability of ALD coating materials for food contact was evaluated according to regulations and recommendations. The coatings of plastic food contact materials are not yet covered by EU legislation and therefore also other substances than mentioned in the list of authorized substances may be used. However, in this case, all the ALD coatings deposited onto the polymer films, e.g. aluminum oxide (Al_2O_3), zinc oxide (ZnO) and titanium dioxide (TiO_2) are authorized to be used in plastic FCMs as an additive or a polymer production aid without specific restrictions (Table 9). The only generic limitation related to the use of these substances is mentioned in Annex II of the Plastics Regulation: the specific migration limit for zinc is given (25 mg/kg food). For the other compounds, Al_2O_3 and TiO_2, the applicable limit could be the generic limit for inertness (limit for overall migration) typically applied for plastic materials. This limit is based on the Framework regulation and requirement that FCMs should not cause changes in the food. Plastic materials should not release their constituents more than 10 mg/dm^2 of its surface area (or 60 mg/kg food).

Table 8. Examples of commercial polymer films used as substrates for ALD and currently available information on their food contact status. From data sheets and statements.

Material & producer	Food contact status & regulations met	Food & conditions of use	Additional information
BOPP Innovia Films	Complies with EU & US legislation for most applications. Details in Declaration of Compliance	**Food types:** Water containing foods (pH>4.5) Acidic foods (pH<4.5) Alcoholic cont. foods (≤50% v/v) Fat containing food Milk, fermented products, cream Dry foods **Conditions of use:** At temperatures up to 40°C without restriction on contact time, including refrigerated and frozen storage Between 40 and 70°C up to 2 h Between 70 and 100°C up to 15 min, including hot fill Product intended to temperature range 0 to 40°C, temperatures below -30 °C or above +70°C not recommended.	When requested: 1) Decl. of comp. 2) Lit. reference 3) Health & safety inf. Food packer has responsibility to verify suitability of final material for intended food contact application, including physical properties, migration and organoleptic properties.
BOPLA (heat seal) BI-AX Int.	Meets EU Regulation 1935/2004 and Plastic directive 2002/72/EC	"All food types under all temperature conditions".	Manufacturer of finished food-contact article has responsibility to ensure compliance with overall migration limit set forth in the Plastics Directive. (60 mg/kg food or 10 mg/dm^2 of material).
BOPLA (plain & heat seal film) BI-AX Int.	"May be used in contact with food in compliance with U.S. Federal Food, Drug, and Cosmetic Act and all applicable food additive regulations, provided that..". **Use and storage conditions** defined in detailed.	Plain film: Only Conditions of Use B (Boiling water sterilized) through H (Frozen or refrigerated storage: Ready-prepared foods intended to be reheated in the container at time of use); Heat seal film: Only under Conditions of Use C (Hot filled or pasteurized above 150 °F) through G (Frozen storage - no thermal treatment in container)	

Table 9. Food contact status of ALD coatings according to regulations in EU and in U.S.

Formula	CAS	Food contact status (EU)	Food contact status (U.S.)
Al_2O_3	1344-28-1	Regulation (EU) No 10/2011	§ 73.575 and 73.1575
ZnO	1314-13-2	Regulation (EU) No 10/2011	§ 182.8991
TiO_2	13463-67-7	Regulation (EU) No 10/2011	§ 73.575 and 73.1575

In U.S. Al_2O_3 is found to be as safe for food use. According to FDA it can be used for coloring foods. ZnO is considered to belong to substances generally recognized as safe (GRAS) when used in accordance with good manufacturing practice. It can be also used, for example, as nutritional dietary supplement in animal feeds and in colorants for polymeric coatings. Synthetic TiO_2 can be used as colorant in foods and drugs. The purity requirements are specified. A maximum amount of TiO_2 is restricted to be below 1 % by weight of the food.

Typical precursors for ALD coatings are presented in Table 10. Trimethylaluminum (TMA) and diethyl zinc (DEZ) were used for Al_2O_3 and ZnO, respectively. In addition, titanium tetrachloride is typically used for TiO_2. Oxidizing precursors were water and ozone. Ethylene glycol and glycerol can be used in inorganic-organic hybrids. Ethylene glycol, glycerol and water are authorized for manufacturing of plastic FCMs. They can be used as an additive or a polymer production aid, and as well as a monomer or other starting substance. Instead, TMA, DEZ and titanium tetrachloride are not authorized for plastic FCMs. However, as mention earlier, plastic food contact materials may contain impurities of non-authorized substances, originating from the manufacturing process and not intended to remain in the final material as is the case with these precursors. However, they should not pose potential health risk to consumers being for example CRM substances. In addition their migration from final food contact material should not exceed 0.01 mg/kg/food. However, these precursors are pyrophoric and thus unstable at ambient environment.

Properties of TMA, DEZ and titanium tetrachloride were studied based on the safety data sheets provided by producers. No component of the commercial products present at levels greater than or equal to 0.1 % is identified as probable, possible or confirmed human carcinogen by International Agency for Research on Cancer (IARC). However, information on germ cell mutagenicity and reproductive toxicity of these chemicals was not available. It would be reasonable to require sufficient tests results needed to ensure the safe use of these substances, for both consumers and employees, from the producer.

Table10. Raw materials for typical ALD layers and their status for food contact in EU/U.S.

Precursors	CAS Number	Food contact status (EU)	Food contact status (FDA)
Trimethyl aluminum	75-24-1	Not authorized	Not authorized
Diethyl zinc	557-20-0	Not authorized	Not authorized
Titanium tetrachloride	7550-45-0	Not authorized	Not authorized
Ethylene glycol	107-21-1	Can be used as additive or polymer production aid, and as monomer or other starting substance. Restriction: SML(T) is 30 mg/kg food.	Not authorized
Glycerol	56-81-5	Can be used as additive or polymer production aid, and as a monomer or starting substance.	§182.1320
H_2O	7732-18-5	Can be used as additive or polymer production aid, and as a monomer or other starting substance.	-
O_2	10028-15-6	-	§173.368, §184.1563

Nor can the precursors used in ALD be found in the database Everything Added to Food in the United States (EAFUS) [39] in which all direct and indirect food additives are collected. Surprisingly ethylene glycol seems also be a non-authorized substance as such. However, several derivatives of ethylene glycol are listed among the authorized substances. Instead, glycerol is recognized as GRAS for several purposes.

ZnO has been tested as an antibacterial additive in composites and in coatings for plastic films. Antibacterial activity in general is promoted by small particles and high surface area. Contact between nanoparticles and bacteria promote antibacterial activity together with reactive oxygen species and release of zinc ions from zinc oxide. Due to the likely antibacterial property, the suitability ALD ZnO coating for food contact was assessed taking in to account the requirements defined in the Regulation (EC) N:o 450/2009.

As mentioned earlier, active and intelligent materials can only be manufactured using substances included in the Community list of authorized substances. An exception makes substances that comply with the relevant food legislation or are separated from food or its surrounding by a functional barrier. The Community list that can be used is still in progress. In 2012 the Commission made available a register of the substances [40] suggested to be included in the list, and for which an application was submitted. The Commission will adopt the list after the EFSA has evaluated the safety of these substances for food contact. For ZnO such an application has not been submitted.

In case ZnO is not separated from food by a functional barrier, relevant food legislation should be followed. Zn and ZnO are not food additives with E codes regulated under EU No 1333. However, Zn and ZnO can be added to food according to regulation EU N:o 1925/2006 in order to restore their content in food after been reduced during manufacturing or storage. Zn and ZnO can also be used in manufacturing food supplements (2002/46/EC). The substrate/passive part of the food package, e.g. packaging material itself, should be in accordance with corresponding EU or national requirements.

7.3 Effect of food simulant on ALD coated polymer films

Several simulants used for testing migration from food contact materials to food were applied to study ALD Al_2O_3 layers on silicon wafer, BOPLA and BOPP in terms of changes in layer properties and migration of aluminum. Al_2O_3 was deposited at 100 ºC (and 80 ºC) using TMA, water/ozone and deposition parameters giving 25 nm on silicon wafer. The Al_2O_3 layers on polymer films were also studied with XPS in order to find out the effect of simulants on the surface chemistry after 10 days exposure to the simulants. In addition, effects on the oxygen barrier of the Al_2O_3 layer were studied before and after the exposure.

Each simulant dissolved Al_2O_3 differently. Effect of water, acidic acid (3%) and ethanol (10%) on thickness of ALD Al_2O_3 layer on silicon wafer was studied as a function of time up to 10 d. Water had no effect on thickness, and thickness after acidic exposure was within the range of deviation. However, with ethanol solution the thickness of the Al_2O_3 layer doubled. Based on SEM images both water and acidic solutions created short “rods” and pores on the surface. These are likely structures remaining after dissolution. In the case of ethanol, the surface was covered with particles which were probably dissolved/precipitated Al salts.

After 10 days of exposure to the simulants the Al content in the BOPP samples remained almost the same, while with the BOPLA the differences were more profound between the three simulants (Figure 11). The acid solution had the strongest effect on the Al_2O_3 layer on the BOPLA. Dissolution must be less uniform with the BOPP than with the BOPLA.

Al_2O_3 can be used in manufacturing of plastic food contact materials and articles as an additive or a polymer production aid without specific restrictions. Migration of Al was small when film samples were exposed to water and ethanol (Figure 12). Instead, exposure to 3 % acetic acid caused significant migration; the highest value was 0.5 mg/dm^2 corresponding to Al_2O_3 migration of 0.9 mg/dm^2. Migration exceeded the limit set for non-authorized substances in all the simulants (1.7 µm/dm^2), but more importantly it was lower than the general limit of overall migration (10 mg/dm^2). Migration was evaluated with ICP/MS by measuring the Al concentration in the simulants after 10 days. The migration of Al was higher when ozone was used as the oxygen source. Acceptable daily intake of Al_2O_3 has not been defined. EFSA has released a scientific opinion on safety of Al and its compounds [41,42].

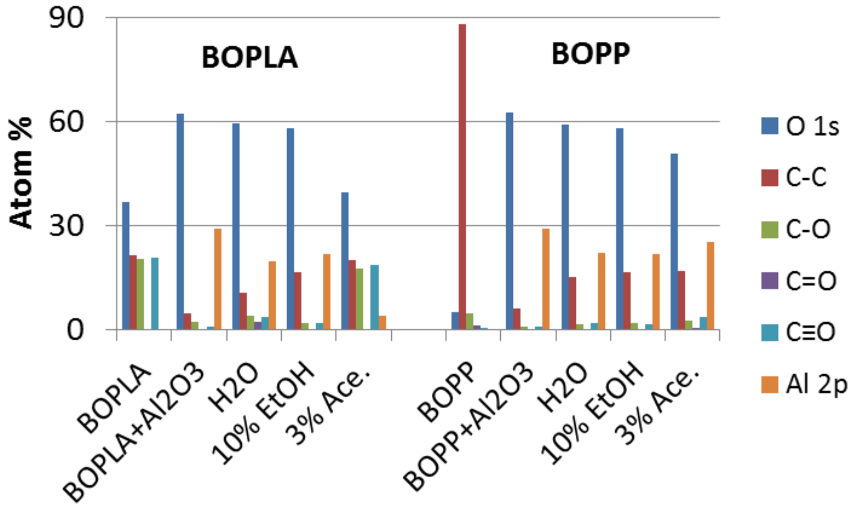

Figure 11. Impact of simulants on sample surface chemistry measured by XPS after 10 d.

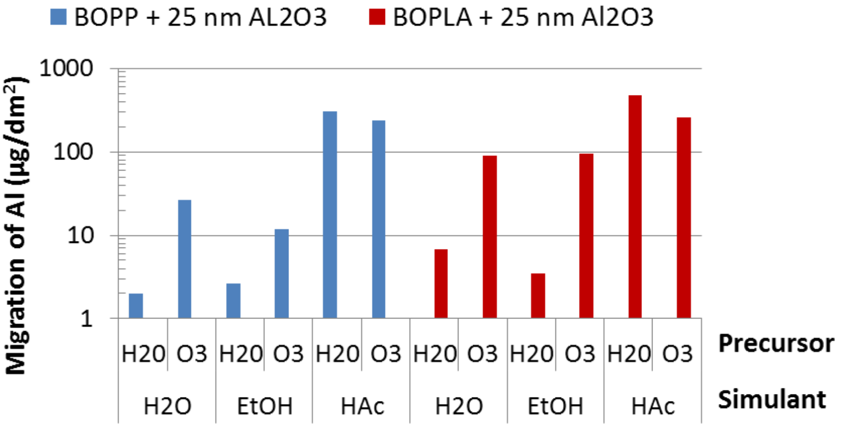

Figure 12. Migration of Al from Al_2O_3 coatings on BOPLA and BOPP measured after 10 d.

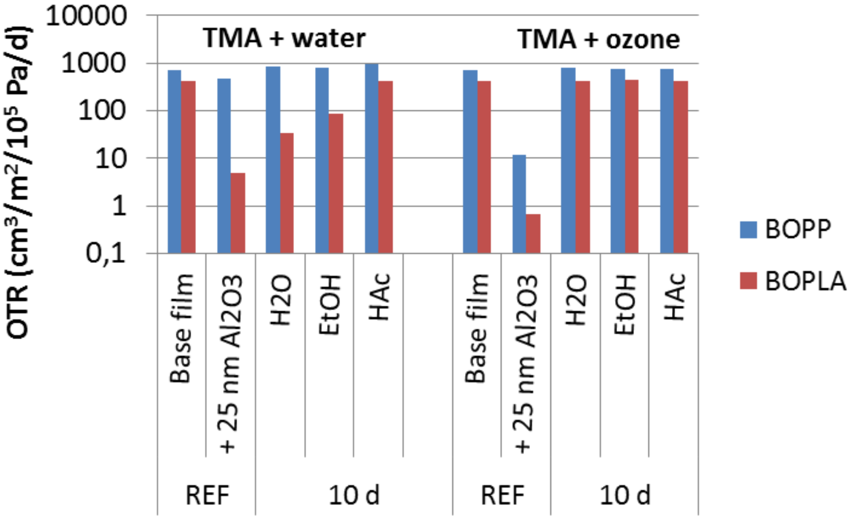

Figure 13. Impact of simulant on OTR of BOPP and BOPLA films with 25 nm of Al_2O_3.

Oxygen barrier was strongly impaired by the exposure to the food simulants due to the tendency of Al_2O_3 to dissolve in the simulants (Figure 13). Initially better gas barrier was observed with BOPLA and ozone as the oxidizing precursor. However, after the exposure the oxygen barrier was better with BOPLA samples deposited with water. With BOPLA the most negative effect was observed with the acid simulant and the least negative with water. Although TiO_2, for example, is less sensitive to dissolution than Al_2O_3, it is obvious that thin metal oxide layers need a top layer to protect them from stresses, to prevent migration, and to act as a sealant. A significant question is then how to obtain defect insensitive films from the roll-to-roll process.

7.4 Occupational safety

Metal-organic precursors, such as TMA and DEZ, and inorganic $TiCl_4$ are pyrophoric, flammable or react violently with water causing burns. All of them cause skin corrosion and thus proper protective clothing and personal protective equipment are crucial. In addition, these chemicals have to be stored in closed metal containers and handled in oxygen free environment. Chemicals have to be duly recorded, handled and stored based on the instructions from the suppliers, required by the law and employer's instructions for work and chemical safety. Likewise, oxidizing precursors, such as ozone, and reaction products from the ALD, such as hydrochloric acid, are hazardous. The entry of such compounds into the research environment has to be prevented by closed systems and purging, and by leading the process gases out with effective ventilation and possible cleaners for the exhaust gases.

Mechanical hazards are possible when removing the reactor for cleaning purposes or even when closing the reactor. Such risks can be avoided by correct procedures and devices assisting in handling the parts to be cleaned, and by proper design of the user interface. In addition, the moving parts are often hot creating a risk for skin burns.

The risk for creating airborne particles when processing and converting coated polymer films was evaluated by measuring the particles released to air when Al_2O_3 coated BOPLA and cellophane films were exposed to abrasive testing. No significant increase in airborne particle count compared to background was observed. The particles were possibly large enough not to be affected by air flows or got attached to the abrased or abrasive surfaces.

ELPI indicated the highest particle count before abrasion and remained approximately constant for the rest of the day. A few higher particle numbers were observed, but they did not coincidence with the abrasion testing. CPC can measure somewhat smaller particles than ELPI. The highest particle count was observed during the lunch break. Abrasive testing increased scatter, but not the average number of particles (Figure 14). The measured values corresponded to particle count in normal room air and were small compared, for example, to air from a nearby urban street.

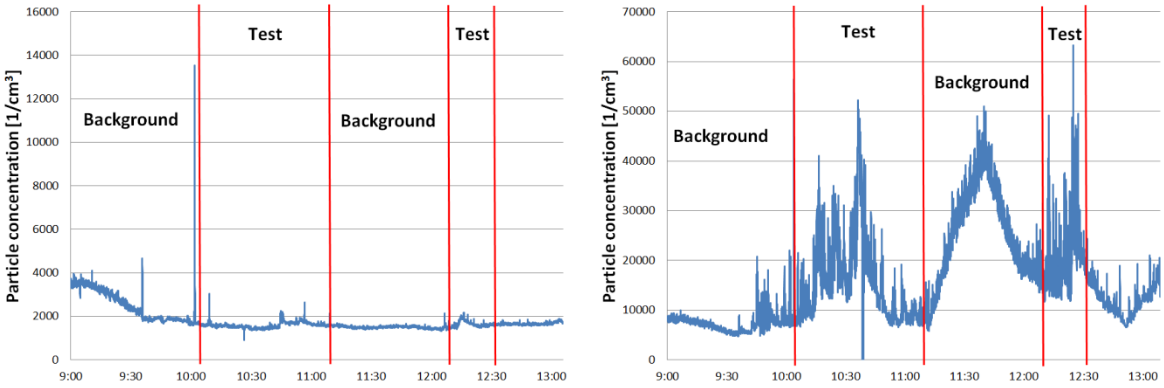

Figure 14. Particle count with ELPI (left) and CPC (right) during the day of abrasion testing.

7.5 Introduction to environmental evaluation

The idea was to study the most important environmental aspects of the life cycle of packaging products which include roll-to-roll ALD process in the value chain. The cradle to gate boundary was selected for the study. The value chain is described in Figure 15.

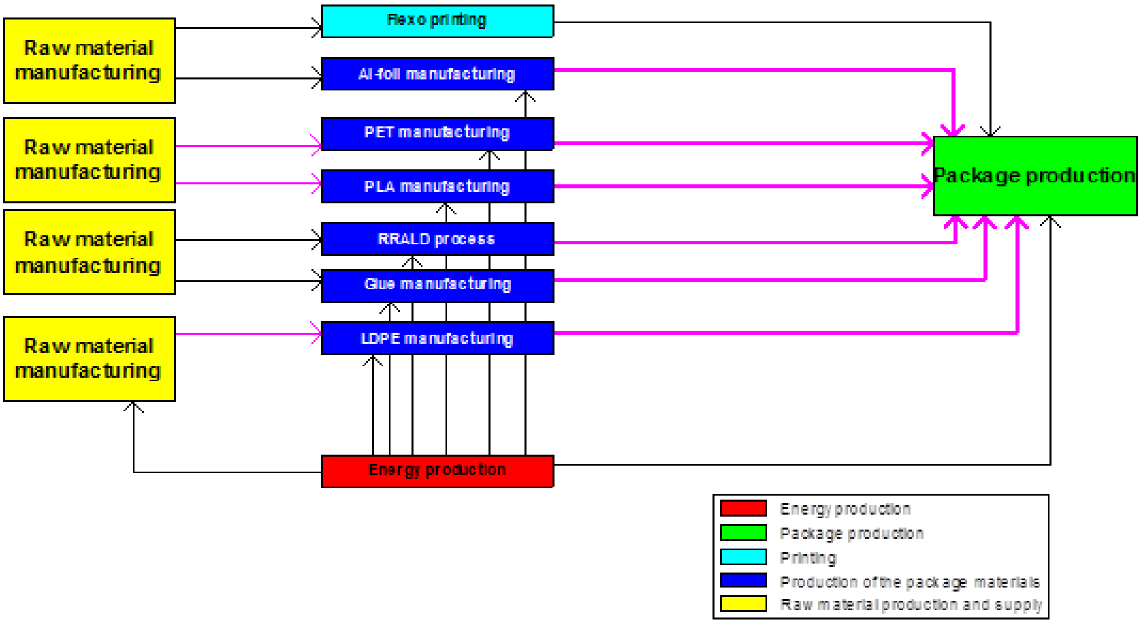

Figure 15. System boundary from cradle to gate for studying the hotspots of package life cycle with RRALD process in the value chain. Colors represent different life cycle stages.

This study was started by defining the structure of the package. The structure of the reference package is described below from outside in. The ALD layer was expected to replace the aluminum foil or metallizing and the second adhesive (marked with asterisk).

- BOPLA or OPET (12-40 µm)
- Printing on reverse (flexo or rotogravure printing)
- Laminating adhesive (2 g/m^2)
- Aluminum foil or metallizing (9 µm) *
- Laminating adhesive or adhesion polymer (2 g/m^2) *
- PLA, OPT or LDPE (12-40 µm)

Some environmental indicators were chosen. Carbon footprint (CO_2 fossil, CH_4, and other greenhouse gases) affect the global warming and climate change. Emissions to air were limited sulphur dioxide (SO_2 equivalent), nitrogen oxides (NO_x), and particles/dust. SO_2 and NO_x cause acidification, eutrophication, photochemical oxidant formation and particulate matter formation, thus affecting both humans and ecosystems, while dust/particles affect the human health. Emissions to water were considered by studying chemical oxygen demand (COD), suspended solids and phosphate ion (PO_4^{3-} eq.) which affect the water quality. Also primary energy consumption and fuels used to produce this energy were studied.

There were several difficulties in data collection and availability. Data was collected successfully from research partners, literature and Ecoinvent regarding the ALD process and production of energy, aluminum foil, rotogravure inks and polymers as such, and emissions from transport. However, no or limited data was obtained, for example, for the production of adhesives and packages, and metallizing. Since the data collection was more or less unsuccessful, it was impossible to perform the calculations and the environmental assessment based on literature and theoretical evaluation of the available data.

7.6 Environmental evaluation of materials and processes

Some LCA results are available for PLA, PET and LDPE granulates. In the case of PLA some studies reduce the amount of carbon bound to the products from the total emissions, but this was neglected since the carbon is released at the end of life –stage either via incineration or degradation. Thus, the numbers shown in Table 11 describe the total emissions from the granulate production only. It is obvious that each of the polymers have their strengths and weaknesses. The converting from granulate to film is not included, and thus both energy demand and emissions would be higher when studying polymer films.

Table 11. Environmental parameters for 1 kg of PLA, PET and LDPE granulates [43-51].

Environmental parameter	PLA granulates	PET granulates	LDPE granulates
Global warming	2.6-2.8 kg CO_2 fossil 5.4-13 g CH_4 0.37-1.1 g N_2O Total: 2.3-3.2 kg CO_2 eq.	2.4 kg CO_2 fossil 12.2 g CH_4 0.03 g N_2O Total: 2.3-2.7 kg CO_2 eq.	1.7 kg CO_2 fossil 16.2 g CH_4 0.02 g N_2O Total 2.1-5.2 kg CO_2 eq.
Gross primary fuels used as fossil depletion	0.24-0.58 kg hard coal 0.06-0.14 kg crude oil 0.38-0.51 kg natural gas Total:0.63-0.92 kg oil eq.	0.22 kg hard coal 0.77 kg crude oil 0.541 kg natural gas Total:1.57 kg oil eq.	0.13 kg hard coal 0.84 kg crude oil 0.773 kg natural gas Total:1.57 kg oil eq.
Emissions – air (g)	7.4-21 g SO_2 eq. 4.6-12.3 g NO_2 3.2-8.8 g dust (PM10 eq.)	8.6-25 g SO_2 eq. 4.3-20 g NO_2 3.0 g dust (PM10 eq.)	7.1-17.4 g SO_2 eq. 3.8 g NO_2 0.7-2.3 g dust (PM10 eq.)
Emissions – water (g)	4.9-6.8 g COD 5.0 kg PO_4^{3-} eq. 0.5-3 g suspended solids	6.0 g COD 2.9 kg PO_4^{3-} eq. 0.5 g suspended solids	2.2 g COD 0.5-1.1 PO_4^{3-} eq. 0.1 g suspended solids
Primary energy consumption	26.3-42.2 MJ fossil 25.6-48.5 MJ renewable Total: 67.8-74.8 MJ	75.4-78.7 MJ fossil 1.5 renewable TOTAL: 76.9-84 MJ	73.0-76.9 MJ fossil 1.2-1.3 MJ renewable Total: 74.3-91.7 MJ

Flexographic and rotogravure printing are commonly used in printing the flexible packaging [52]. There are not many LCA results available for flexo and rotogravure printing, e.g. database Ecoinvent has data concerning printing inks used in these processes. One study reported the energy demand and gas emissions and suggested that “*the average overall flexography GHG emissions impact is 43% lower and the non-renewable energy use is 31% lower than the rotogravure impact*”. However, a wider study of emissions should be performed in order to do final conclusions concerning the printing processes. Several studies find the impact from printing process of packaging to be of minor importance [53,54] in the life cycle of a package. This can be assumed to be the case in this study as well.

Adhesives used for this type of packaging would typically be two component adhesives e.g. polyester/polyurethane. LCA data for certain types of adhesives is available in public databases e.g. Ecoinvent and VTT’s own database EcoData, but information for the type of adhesive needed was not found. The adhesive layers are the thinnest layers in the studied packaging, so the impact could be estimated to be of minor importance in the big picture.

Aluminum foil and metallizing are used in packaging as barrier layers against light, oxygen, moisture, odors, flavors and bacteria. They can also improve the outlook and appearance of the packaging. The thickness of aluminum foil is typically 6 or 9 µm. There are LCA results available for aluminum foil but not many for metallizing. Table 12 describes the total released emissions from aluminum foil production.

Table 12. Environmental parameters per 1 kg of foil collected from literature [55,56].

Environmental parameter	
Global warming	9.0-9.9 kg CO_2 fossil 17.2-19.7 g CH_4 0.14-0.17 g N_2O Total: 9.6-10.4 kg CO_2 eq.
Gross primary fuels used as fossil depletion	1.00-1.06 kg hard coal 0.76-0.83 kg crude oil 0.69-0.9 kg natural gas Total:2.14-2.49 kg oil eq.
Emissions to air (g)	37-49 g SO_2 eq. 16.8-18.9 g NO_2 7.0-12.6 g dust (PM10 eq.)
Emissions to water (g)	1.5-2 g COD 8.5-11.5 g suspended solids
Primary energy consumption	134.9-156.6 MJ fossil 40.6-44.1 renewable Total: 175.5-200.7 MJ

The information concerning roll-to-roll ALD process was collected within the project from Lappeenranta University of Technology (Table 13). The values are estimated based on the trials since the process has not been used for larger amounts of polymer film yet. Data for the polymer film, liquid nitrogen and electricity is available in public databases. However, the evaluation of environmental impacts from the roll-to-roll ALD process would also require data of trimethylaluminum (TMA) production which was not available during the project.

Table 13. Input and output parameters of roll-to-roll ALD process.

Inputs	**Outputs**
1000 kg polymer film	1000 kg ALD-coated polymer film
1000 kg liquid Nitrogen	0.05kg CH_4 to air
0.225 kg $Al(CH_3)_3$	0.1kg Aluminum oxide waste
1.25kg water	heat to water
4.53 MWh electricity	

The information about the package production i.e. combining of the packaging layers was not available in the public databases nor received during the data collection in this project.

7.7 Environmental hotspots

The data collection in this project was found to be more difficult than expected. Several data gaps remained at the end of the project. It was difficult to know for a fact the most important environmental topics in the value chain of the studied packaging. However, since the ALD process would replace aluminum foil or metallizing and the second layer of adhesive, those would be the most interesting aspects to be studied. Unfortunately there were some data gaps in those layers as well so that no final conclusions could be made.

Several studies [57-59] have indicated that the environmental impact of packaging is relevantly low in the value chain of food products, and that the production of food has the highest impact on the environment. The most important function of the packaging is to protect the food. If the packaging does not fulfill its requirements and the food goes bad before it is used, the environmental impact increases further since there is a need for new food and packaging production. Thus the barrier properties of ALD vs. those of aluminum foil or metallizing (or true barrier requirements) are the key question from the environmental point of view. If the performance of the ALD layer is adequate or equal to aluminum foil or metallizing layer, i.e. if the food is protected in both packaging options similarly and for equally long, then the environmental differences between the packaging options become interesting and should be studied further.

8. Conclusions

Aluminum oxide (Al_2O_3) deposited at low temperatures clearly improved the oxygen and water vapor barrier properties of most polymer films studied. The most significant impact was observed with cellulose and polyester films, which indicated the importance of polar oxygen groups. Film additives, such as antioxidants, can prevent completely the growth of an Al_2O_3 layer when using the trimethylaluminum/water deposition process. Likewise, the polymer coatings on fiber-based webs have to be uniform and defect-free prior to atomic layer deposition (ALD).

The growth of an Al_2O_3 layer on polymers starts through sorption of a metal-organic precursor onto and into the polymer followed by chemical interactions with the polar oxygen groups and a possible formation of an interphase. This is followed by cluster formation and further layer growth through clusters. Polar oxygen group enhance thin layer coverage. Cluster formation is more obvious with hydrophobic polymers and these clusters can affect the surface topography even after the surface is totally covered with Al_2O_3.

Surface chemistry of polymer films has an impact on thin layer growth, structure and eventually final functional properties. Therefore, it is no surprise that corona and plasma pre-treatments can improve the barrier properties of thin layers. However, it is important, as with polymer films to be e.g. metallized, to prevent the pre-treated polymer film from attracting contaminants prior to the ALD process.

The reactor temperature should be as high as possible and yet lower than the temperature at which the polymer degrades, melts or softens. ALD at a too low temperature would typically require longer exposure and purge times and thus increased overall cycle times.

Choice of oxygen source (water vs. ozone) is an additional tool to affect thin layer growth and final functionality of thin layers. The high oxidizing power of ozone can also be used to activate difficult polymer surfaces by pulsing ozone into the reactor prior to the normal ALD process. Use of ozone often leads also to a better oxygen barrier, but to a similar or impaired water vapor barrier. This is likely due to a more uniform, but also a more polar oxide layer. Likewise, the final barrier properties of oxide layers can be improved by prolonging the initial deposition cycle.

Flexibility is a key requirement for several packaging materials. Although chemically favorable surfaces for ALD also improve the mechanical properties of polymer films with thin oxide layers, the thin layer has to be protected from mechanical stresses with an additional polymer layer. The mechanical properties of thin layers can be improved by combining inorganic oxide and inorganic-organic hybrid layers into a nanolaminate. Flexibility of a nanolaminate increases when the thickness of the individual Al_2O_3 layers decreases and the hybrid is used as a spacer between the oxide layers.

A direct contact between the thin oxide layer (Al_2O_3 or ZnO) and the bacteria promotes antimicrobial activity, although migration of antimicrobial compounds was also observed for layers deposited at low temperatures. All the samples tested showed antimicrobial activity against *E. coli*. The standard testing protocols applied were appropriate to study antimicrobial activity of ALD layers and nanolaminates.

Based on our analyses a uniform ALD Al_2O_3 barrier layers do not fall under the European Commission's definition of nanomaterial. Instead, ALD grown layers resemble the metallized layers used in food packages for tens of years. Plastic materials should not transfer their constituents to food in quantities exceeding 10 mg/dm^2 of food contact surface. Although migration of Al_2O_3 from the ALD layer to specific food simulants was significantly lower, the oxygen barrier was strongly impaired due to the tendency of Al_2O_3 to dissolve in the simulants. It is obvious that polymer films coated with thin oxide layers require a top layer to protect them from stresses, to prevent migration, and to act as a sealant.

There are also several occupational safety issues. The typical precursors are pyrophoric, flammable or react violently with water causing burns. Likewise, oxidizing precursors and reaction products from the ALD can be hazardous. Mechanical hazards are possible when removing the reactor for cleaning purposes or even when closing the reactor. In addition, the moving parts are often hot creating a risk for skin burns. The risk for creating airborne particles when processing and converting coated polymer films was also evaluated. No significant increase in airborne particle count compared to background was observed.

The data collection for the environmental hotspot analysis was more difficult than expected. There were data gaps so that no final conclusions could be made. Several studies have indicated the environmental impact of packaging to be relevantly low in the food product value chain. If the performance of the ALD layer is adequate compared to competing solutions, then the environmental differences between the packaging options become interesting and should be studied further.

References

1. Leskelä, M., Ritala, M. 2002. Atomic layer deposition (ALD): from precursors to thin film structures. Thin Solid Films 409(1), pp. 138-146.

2. George, S.M. 2010. Atomic layer deposition: an overview. Chemical Reviews 110(1) pp. 111-131.

3. Puurunen, R. 2005. Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process, Journal of Applied Physics 97 121301.

4. Directive 2001/95/EC, p. 4, Accessed 8.7.2013: http://eurlex.europa.eu/LexUriServ/-LexUriServ.do?uri=CONSLEG:2001L0095:20100101:EN:PDF

5. Wilson, C.A., Grubbs, R.K., George, S.M. 2005. Nucleation and growth during Al_2O_3 atomic layer deposition on polymers. Chem. Mater. 17(23) pp. 5625-5634.

6. Spagnola, J.C., Gong, B., Arvidson, S.A., et al. 2010. Surface and sub-surface reactions during low temperature aluminium oxide atomic layer deposition on fiber-forming polymers J. Mater. Chem. 20(20) pp. 4213-4222.

7. Gong, B., Parsons, G.N. 2012. Quantitative in situ infrared analysis of reactions between trimethylaluminum and polymers during Al_2O_3 atomic layer deposition J. Mater. Chem. 22(31) pp. 15672-15682.

8. Puurunen, R.L. 2005. Correlation between the growth-per-cycle and the surface hydroxyl group concentration in the atomic layer deposition of aluminum oxide from trimethylaluminum and water. Appl. Surf. Sci. 245(1-4) pp. 6-10.

9. Grigoras, K., Franssila, S., Airaksinen, V.M. 2008. Investigation of sub-nm ALD aluminum oxide films by plasma assisted etch-through. Thin Solid Films 516(16) pp. 5551-5556.

10. Puurunen, R. Vandervorst, W., Besling, W., et al. 2004. Island growth in the atomic layer deposition of zirconium oxide and aluminum oxide on hydrogen-terminated silicon: Growth mode modeling and transmission electron microscopy. J. Appl. Phys. 96(9) pp. 4878-4889.

11. Tuominen, M. 2012. Atmospheric plasma modification in extrusion coating, Tampere University of Technology. Publication 1065. Tampere, Finland.

12. Hirvikorpi, T., Vähä-Nissi, M., Nikkola, J., et al. 2011. Thin Al_2O_3 barrier coatings onto temperature-sensitive packaging materials by atomic layer deposition. Surf. Coat. Technol. 205(21-22) pp. 5088-5092.

13. Mrkic, S., Galic, K., Ivankovic, M. 2007. Effect of temperature and mechanical stress on barrier properties of polymeric films used for food packaging. J. Plast. Film Sheet., 23(3) pp. 239-256.

14. Groner, M.D., Fabrequette, F.H., Elam, J.W., et al. 2004. Low-temperature Al_2O_3 atomic layer deposition. Chem. Mater. 16(4) pp. 639-645.

15. Miller, D.C., Foster, R.F., Zhang, Y., et al. 2009. The mechanical robustness of atomic-layer- and molecular-layer-deposited coatings on polymer substrates. J. Appl. Phys. 105 pp. 093527-1 – 093527-12.

16. Zhang, Y., Yang, R., George, S.M., et al. 2011. In-situ inspection of cracking in atomic-layer-deposited barrier films on surface and in buried structures. Thin Solid Films 520(1) pp. 251-257.

17. Xie, Y., He, Y., Irwin, P.L., et al. 2011. Antibacterial activity and mechanism of action of zinc oxide nanoparticles against *Campylobacter jejuni*. Appl. Environ. Microbiol. 77(7) pp. 2325-2331.

18. Jiang, J., Li, G., Ding, Q., et al. 2012. Ultraviolet resistance and antimicrobial properties of ZnO-supported zeolite filled isotactic polypropylene composites. Polym. Degrad. Stab. 97(6) pp. 833-836.

19. Li, X., Xing, Y., Jiang, Y., et al. 2009. Antimicrobial activities of ZnO powder-coated PVC film to inactivate food pathogens, Int. J. Food Sci. Technol. 44(11) pp. 2161–2168.

20. Li, X.H., Xing, Y.G., Li, W.L., et al. 2010. Antibacterial and physical properties of poly(vinyl chloride)-based film coated with ZnO nanoparticles. Food Sci. Tech. Int. 16(3) 225-232.

21. Choi, D.-W., Kim, S.-J., Lee, J.H., Chung, K.-B., Park, J.-S. 2012. A study of thin film encapsulation on polymer substrate using low temperature hybrid ZnO/Al_2O_3 layers atomic layer deposition, Current Applied Physics 12 pp. 19-23.

22. Lee, S.-M., Grass, G., Kim, G.-M., Dresbach, C., Zhang, L., Gösele, U., Knez, M. 2009. Low- temperature ZnO atomic layer deposition on biotemplates: flexible photocatalytic ZnO structures from eggshell membranes, Phys. Chem. Chem. Phys. 11(19) pp. 3608–3614.

23. Narayan, R.J., Adiga, S.P., Pellin, M.J., et al. 2010. Atomic layer deposition of nanoporous biomaterials. Materials Today 13(3) pp. 60-64.

24. Narayan, R.J., Adiga, S.P., Pellin, M.J., et al. 2010. Atomic layer deposition-based functionalization of materials for medical and environmental health applications. Phil. Trans. R. Soc. A 368(1917) pp. 2033-2064.

25. Luka, G., Godlewski, M., Guziewicz, E., et al. 2012. ZnO films grown by atomic layer deposition for organic electronics, Semicond. Sci. Technol. 074006 27(7) 7 pp.

26. Malm, J., Sahramo, E., Perälä, J., et al. 2011. Low-temperature atomic layer deposition of ZnO thin films: Control of crystallinity and orientation. Thin Solid Films 519(16) pp. 5319-5322.

27. Elam, J.W., Sechrist, Z.A., George, S.M. 2002. ZnO/Al2O3 nanolaminates fabricated by atomic layer deposition: growth and surface roughness measurements. Thin Solid Films 414(1) pp. 43-55.

28. Ott, A.W., Chang, R.P.H. 1999. Atomic layer-controlled growth of transparent conducting ZnO on plastic substrates, Mat. Chem. Phys. 58(2) pp. 132-138.

29. Regulation EC No 1935/2004, p. 4, Accessed 19.4.2013, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2004R1935:20090807:EN:PDF

30. Regulation EC No 2023/2006, p. 75. Accessed 19.4.2013 http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2006R2023:20080417:EN:PDF

31. Regulation EU No 10/2011, p. 1. Accessed 23.4.2013 http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2011R0010:20130101:EN:HTML

32. Regulation EC No 282/2008, March 27, 2008.

33. Directive 2007/42/EC, June 29, 2007.

34. Directive 84/500/EC, Amended April 29, 2005.

35. Regulation EC 450/2009, May 29, 2009.

36. Recommendation 2011/696/EU, Accessed 19.4.2013, http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:275:0038:0040:EN:PDF

37. Schupp, B. 2013. Food Contact Materials. Regulatory approaches in the food contact sector. Special focus: Active and Intelligent Materials. 26th IAPRI Symposium on Packaging, VTT Technical Research Centre of Finland, Espoo, Finland.

38. EFSA Opinion. 2007. Opinion of the Scientific Panel on food additives, flavourings, processing aids and materials in contact with food (AFC). The EFSA Journal 452 to 454, pp. 1-10.

39. Everything Added to Food in the United States (EAFUS). FDA. Accessed 8.7.2013: http://www.accessdata.fda.gov/scripts/fcn/fcnNavigation.cfm?filter=&sortColumn=&rpt=eafusListing

40. European Commission. 2012. Active and intelligent materials and articles: European Commission. Register of substances for which a valid application for authorisation was submitted under Regulation EC No 450/2009. Accessed 24.4.2013: http://ec.europa.eu/food/food/chemicalsafety/foodcontact/docs/ec_register_active_intelligent_en.pdf

41. EFSA Opinion. 2008. Safety of aluminium from dietary intake. The EFSA Journal 754, p. 1-34.

42. EFSA Opinion. 2008. Annex of the opinion Safety of aluminium from dietary intake. The EFSA Journal 754, p. 1-88.

43. Vink, E., Davies, S., Kolstad, J. 2010. The eco-profile for current Ingeo® polylactide production. Industrial Biotechnology. 6(4) pp.212-224.

44. Groot, W., Borén, T. 2010. Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand. International Journal of Life Cycle Assessment. Vol 15(9) pp. 970-984.

45. Ecoinvent database, unit process Polylactide, LCI data

46. Gironi, F., Piemonte, V. 2011. Life Cycle Assessment of Polylactic Acid and Polyethylene Terephthalate Bottles for Drinking Water. Environmental Progress & Sustainable Energy 30(3) pp. 459-468.

47. Ncube, A., Borodin, Y. 2012. Life Cycle Assessment Of Polyethylene Terephthalate Bottle. 7th International Forum on Strategic Technology (IFOST). Tomsk, Russia, 18.-21. September 2012.

48. Ecoinvent database, unit process Polyethylene terephthatalate, granulates, amorphous, LCI data.

49. Anonymous. 2008. Low density polyethylene (LDPE), Environmental Product Declarations of the European Plastics Manufacturers. Plastics Europe. Available online at http://www.plasticseurope.org/Documents/Document/20100312112214-FINAL_LDPE_270409-20081215-018-EN-v1.pdf.

50. Patel, M., Bastioli, C., Marini, L., Würdinger, E. 2005. Life-cycle Assessment of Bio-based Polymers and Natural Fiber Composites. Biopolymers Online.

51. Ecoinvent database, unit process LDPE granulates, LCI data.

52. Veith, S., Barr, S. 2008. Life cycle assessment: Flexographic and Rotogravure printing comparison & Flexographic plate imaging technologies. DuPont Engineering and Research Technology (DuET).

53. Varžinskas, V., Staniškis, J. Lebedys, A., et al. 2009. Life Cycle Assessment of Common Plastic Packaging for Reducing Environmental Impact and Material Consumption. Environmental Research, Engineering and Management 4(50) pp.57-65

54. Gravure, The environmentally friendly print process. Gravure news 166/07. Available online at http://www.era.eu.org/04/downloads/ERA_env_gravure.pdf.

55. Environmental Profile Report for the European Aluminium Industry. Life Cycle Inventory data for aluminium production and transformation processes in Europe. European aluminium association. 2008.

56. GaBi database, unit process Aluminium foil, LCI data.

57. Katajajuuri, J-M., Grönroos, J., Usva, K., et al. 2006. Broilerin fileesuikaleiden tuotannon ympäristövaikutukset ja kehittämismahdollisuudet. MTT. Tampereen yliopistopaino Oy – Juvenes print. 118 p.

58. Silvenius, F., Katajajuuri, J-M., Grönman, K., et al. 2012. Pakkausten ympäristövaikutukset elintarvikeketjussa. Maataloustieteen Päivät 2012.

59. Environmental Impact of Packaging in the UK Food Supply System. INCPEN 1996. Available online at http://www.incpen.org/docs/Foodsupply.pdf.