



TAMPERE UNIVERSITY OF TECHNOLOGY

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**UTILIZATION OF ATOMIC LAYER DEPOSITION IN PACKAGING  
STRUCTURES**

Licentiate Thesis

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D.Sc. (Tech.) Mika Vähä-Nissi.  
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## ABSTRACT

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Nowadays, a lot of attention is focused on the possibilities for using Atomic Layer Deposition (ALD) process in packaging solutions. The greatest benefit of an ALD layer is the loss of weight to the packaging. This leads to cost savings during the packaging life cycle. The main target concerning packaging solutions is to create a profitable way to manufacture an ALD layer to packages. At the moment, the most applicable solution seems to be the development of Roll-to-Roll ALD (RRALD) process being faster and cheaper than the batch ALD process.

In this thesis the ALD process is first explained briefly. Then the materials in the process are presented followed by comparison between different ALD processes. Finally, the benefits of using ALD in packaging technology and new ideas about possible solutions based on ALD are discussed.

Results indicate, that a few nanometers thick aluminum oxide layer produced by ALD can improve water vapour and oxygen barrier significantly, when this layer is deposited onto a polymer substrate. On polyethylene terephthalate (PET) surface and in the best scenario, an  $\text{Al}_2\text{O}_3$  ALD layer decreased moisture and oxygen permeation through the structure to one percentage of the original value. On top of polyolefins, such as low density polyethylene and polypropylene (LDPE and PP, respectively), and polylactic acid (PLA) the  $\text{Al}_2\text{O}_3$  ALD layer decreased the measured moisture and oxygen permeation through the structure tens of times lower level compared to the value of polymer only. An  $\text{Al}_2\text{O}_3$  ALD layer no thicker than 40 – 50 nm is enough to improve the water vapor permeation of LDPE, PP and PET films less than  $1 \text{ g/m}^2/24\text{h}$  in normal conditions. A film with a top  $\text{Al}_2\text{O}_3$  ALD layer can be further extrusion coated with an extra LDPE layer to create a structure with excellent sealing properties.

Currently RRALD process might be a slightly more expensive way to produce packaging than the conventional laminating process, but there will be savings in terms of material and transportation costs (empty packages, packaging with the product and packaging eventually as litter). Packaging in which aluminum foil is replaced by an ALD layer can also be recycled and thus avoid ending up in a landfill.

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Nykyään ollaan kiinnostuneita rullalta rullalle tuotetun atomikerroskasvatuksen (ALD) mahdollisuuksista massatuotantoon perustuvissa pakkausratkaisuissa. ALD kerroksella mahdollistetaan pakkausmateriaalien kerrospaksuuksien ohentaminen ja joissain tapauksissa joidenkin kerrosten poistaminen. Tämä johtaa materiaalisäästöihin pakkauksen elinkaaren aikana. Pakkaussovelluksissa suurin haaste on kehittää taloudellisesti kannattava tuotantotapa. Tällä hetkellä ainoa varteenotettava tapa näyttää olevan rullalta rullalle tehtävä ALD prosessi, joka on tarpeeksi nopea ja kustannustehokas.

Tutkimuksessa on läpikäyty ALD prosessi lähtö- ja loppumateriaaleineen. Lopuksi on esitelty saavutettuja tuloksia ja pohdittu tulevaisuuden mahdollisuuksia ALD tekniikan hyödyntämiseksi pakkausratkaisuissa.

Tässä työssä saavutettiin ALD tekniikalla tuotetulla, muutamien kymmenien nanometrien paksuisella, alumiinioksidikerroksella merkittävästi paremmat vesihöyry- ja happitiiveysominaisuudet polymeerikalvolle. Polyeteenitereftalaatin (PET) pinnalla  $\text{Al}_2\text{O}_3$  ALD kerros paransi parhaimmillaan vesihöyryn- ja hapenläpäisyä noin sadasosaan. Polyolefiinien, pientiheyspolyeteenin ja polypropeenin (LDPE ja PP) sekä polymaitohapon (PLA) pinnalla kyseiset tiiveysominaisuudet tippuivat ALD kerroksen ansiosta muutamia kymmeniä kertoja matalammalle tasolle suhteessa pelkkään kalvoon.  $\text{Al}_2\text{O}_3$  ALD kerroksen tarvitsee olla vain 40 – 50 nm paksu, jotta LDPE, PP tai PET kalvon vesihöyrynläpäisy saadaan alle  $1 \text{ g/m}^2/24\text{h}$ :an normaaleissa olosuhteissa. Polymeerin pinnalla olevan  $\text{Al}_2\text{O}_3$  ALD kerroksen päälle voidaan ekstruusiopäällystää LDPE kerros luomaan rakenteelle hyvät saumausominaisuudet.

Rullalta rullalle tuotettu ALD prosessi on vielä tänä päivänä huomattavasti kalliimpi kuin perinteinen laminointi, mutta säästöjä kertyy pakkauksen valmistuksen jälkeen, koska pakkaus on kevyempi ja ympäristöystävällisempi. Jos pakkauksen alumiinikerros korvataan  $\text{Al}_2\text{O}_3$  ALD kerroksella, voi tuote muuttua kaatopaikalle menevästä jätteestä kierrätettäväksi materiaaliksi.

## PREFACE

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The supervisor of my postgraduate studies and one examiner of this licentiate thesis Professor Jurkka Kuusipalo and other examiner D.Sc. (Tech.) Mika Vähä-Nissi deserves my special thanks for all their efforts.

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Tampere, October 2014

Petri Johansson

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**TERMS AND DEFINITIONS**

<b>Al(CH<sub>3</sub>)<sub>3</sub></b>	trimethylaluminum (TMA)
<b>ALD</b>	atomic layer deposition
<b>Al<sub>2</sub>O<sub>3</sub></b>	aluminum oxide
<b>CH<sub>4</sub></b>	methane
<b>CVD</b>	chemical vapor deposition
<b>H</b>	hydrogen
<b>H<sub>2</sub>O</b>	water
<b>(LD)PE</b>	(low density) polyethylene
<b>N<sub>2</sub></b>	nitrogen (typically purge gas in ALD cycle)
<b>OTR</b>	oxygen transmission rate
<b>O<sub>3</sub></b>	ozone
<b>PET</b>	polyethylene terephthalate
<b>PLA</b>	polylactic acid
<b>PP</b>	polypropylene
<b>PRECURSOR</b>	gas, which reacts with substrate in the ALD process
<b>SEALABILITY</b>	how a material can be sealed at itself (required temperature, etc.)
<b>TG</b>	glass-transition temperature
<b>TiO<sub>2</sub></b>	titanium dioxide
<b>TMA</b>	trimethylaluminum [Al(CH <sub>3</sub> ) <sub>3</sub> ]
<b>WVTR</b>	water vapor transmission rate

# 1 INTRODUCTION TO ALD TECHNOLOGY

The idea of using ALD technology for packaging solutions is based on economic benefit. Environmental protection, including this idea of using ALD technology, will give considerable back up. Such a new technology has a potential for reducing waste dramatically. Today there is a trend towards more sustainable and light weight packages. The biggest benefit of the ALD process in packaging structures is the loss of weight. When using a substantially better barrier layer than polymer, the amount of polymer in the structure can be decreased. Light weight packaging materials enable both material savings and lower transport costs. Another advantage over present-day packages is recyclability. Without an aluminum layer in the structure, recycling of the package can be carried out easily. Using the ALD process in a mass production of packaging materials is a future target due to currently too high unit costs.

Many researchers around the world are working hard to make the production of ALD layer more cost efficient. There is also competition between companies, who will be the first on the market with a techno-economically feasible process, because package markets all over the world are eager to replace current solutions.

ALD is a process where thin films of material are deposited one atomic layer at a time. The main advantage of ALD is a uniform and pinhole-free film, which can be obtained regardless of the shape of the substrate. The ability to perform roll-to-roll ALD coating would open huge possibilities for this technique as high barrier layers are needed to avoid the diffusion of liquids and/or gases through webs, for example, in the food packaging industry.

The purpose of the ALD process is to produce a conformal, solid, thin layer film from at least two gaseous precursors. ALD is based on chemical reactions on the surface of the processed substrate. The substrate is exposed to only one precursor gas at a time. The excess precursor, which has not reacted with the substrate, is always purged from the system before the next precursor gas is fed in. So a complete ALD cycle consists of four stages (precursor A, purge, precursor B and purge).

After one ALD cycle, one layer of desired coating is bonded on the substrate surface. The obtained layer is typically ~0.1 nm thick. A typical ALD coating is made through several such reaction cycles and the total layer thickness varies from 1 to 100 nm. Thus, about 100 ALD cycles are needed to achieve the thickness of 10 nm. [1, 2]

## 2 MATERIALS IN ALD PROCESS

The materials used in the ALD process include the produced material in the process and the base material. The produced material in the ALD process is attached to the substrate by chemical bonding.  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  are the most commonly produced layers in the ALD process, but only  $\text{Al}_2\text{O}_3$  is used in this thesis.

### 2.1 Precursors and Layers

All the materials produced in the ALD process have a specific function in the final product. For example, the role of oxide films may be for dielectrics or for barrier applications. This thesis concentrates on new possibilities of ALD solutions in packages. The main role of an ALD layer in packaging is to achieve better barrier properties.

Figures 2a, 2b, 2c 2d and 2e demonstrate the chemical reactions in the ALD process. TMA (trimethylaluminum) and water are used as the precursors in the ALD process with chemical bonding between molecules on top of the substrate [3]. First the substrate with hydroxyl surface groups ( $-\text{OH}$ ) is exposed to the first precursor, TMA [ $\text{Al}(\text{CH}_3)_3$ ]. The process releases methane [ $\text{CH}_4$ ] which is flushed away. Then the surface of dimethyl aluminum ( $-\text{Al}(\text{CH}_3)_2$ ) is exposed to the second precursor i.e. water [ $\text{H}_2\text{O}$ ]. Finally, the released methane is again flushed away with excess water vapor. As a result an  $\text{Al}_2\text{O}_3$  layer is formed. The process can now be started again from the beginning and can be repeated as many times as necessary. [3]

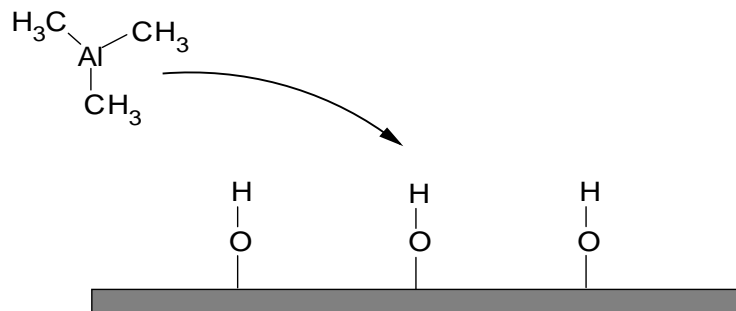


Figure 2a. Substrate with hydroxyl ( $-\text{OH}$ ) -groups is exposed to first precursor, TMA.



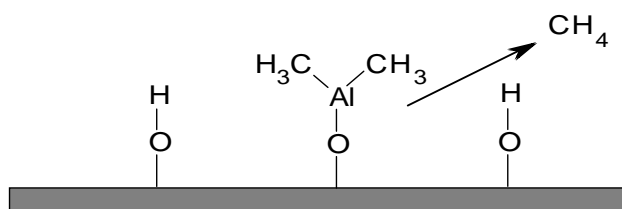


Figure 2b. Methane and excess TMA are flushed away.

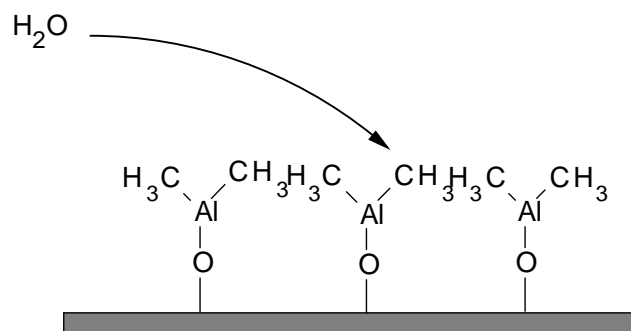


Figure 2c. Dimethyl aluminum -substrate is exposed to second precursor, water.

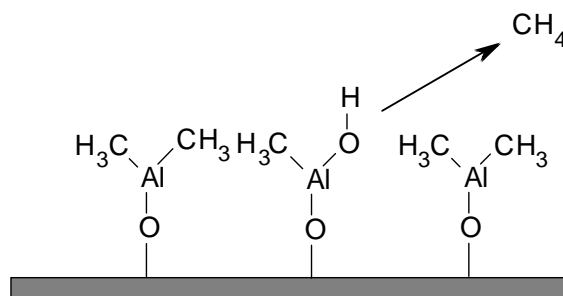


Figure 2d. Methane and excess water are flushed away.

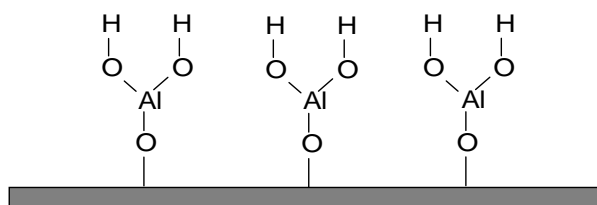


Figure 2e. The Al<sub>2</sub>O<sub>3</sub>-layer is formed. The process can now be repeated.

## 2.2 Substrates

The producing technology of packaging must be fast and effective due to economical constraints. This is why roll-to-roll solution is the only reasonable manner to produce packaging materials. Because the material has to be suitable for winding, it has to stand bending without any damage. This will exclude many materials and solutions out of the scope.

The most important functions of a typical package are:

- 1 to provide a physical protection to the product, but be as light and small as possible
- 2 to create an appropriate barrier layer between inside and outside of the package
- 3 to provide information both about the product and the package
- 4 to have suitable design and to encourage potential buyers to purchase the product
- 5 to give the required shelf life to the product

The aluminum is one of the layer materials in the ALD technology. The layer is in nano scale and thus so thin that it does not necessarily impair recycling. An ALD layer can replace or reduce much thicker materials in packaging structure. The main packaging materials today are fiber, polymer, glass and metal.

Glass is not suitable because packaging materials in mass production must be used for roll-to-roll solutions. Glass will break up when rotating it.

The base material in the ALD process has to be a solid and preferably nonporous surface, because precursor gases can penetrate into the pores and not necessarily participate in creating a uniform layer on the surface of the substrate. Thus, uncoated fiber based materials are generally not feasible for the ALD process.

Metal is an excellent barrier material as such. ALD coating is capable to replace metal as a barrier. A juice can is good example, where ALD layer can replace the aluminum foil in the packaging structure.

Polymers are the materials of interest to focus. LDPE is the most commonly used polymer in packaging applications [4]. It has a good water vapor barrier and excellent heat sealability, but it is a poor oxygen barrier material [5]. In future, the popularity of biomaterials (e.g. PLA) is also expected to increase. A lot of research work is being carried out concerning biopolymers and recyclable polymers. In this thesis is also studied PET and PP.

### 3 ALD PROCESS SOLUTIONS

Batch and continuous ALD process devices are easy to manufacture, because it is simple to create vacuum. Roll-to-Roll ALD devices are a huge challenge, where low pressure is needed for the ALD process between unwinding and rewinding.

#### 3.1 Batch ALD (BALD)

The ALD layer is traditionally applied to stationary substrates not moving during the ALD process. This is called a batch process. Batch ALD is still by far the most popular ALD technology today, because Roll-to-Roll technology is not yet ready for a commercial use. The product has to be valuable enough, if the batch ALD process is to be used. The added cost due to the ALD process has to be so small in order not to make a significant increase to the total price of the product. A good example is an OLED television, where a batch ALD technology can be used to produce the screen, because the whole TV is so expensive compared to the costs of the screen only. [6]

As far as polymer surfaces are concerned, there are many articles where the effect of BALD coating on the WVTR and OTR has been studied. Al<sub>2</sub>O<sub>3</sub> BALD coating on polymer surface can improve the WVTR and OTR significantly. How much depends on the material and process parameters used as demonstrated in tables 3.1, 3.2 and 3.3.

Table 3.1. Water vapor and oxygen barrier with various structures [7].

	WVTR [g/m <sup>2</sup> /day]		OTR [cm <sup>3</sup> /m <sup>2</sup> /10 <sup>5</sup> Pa/day]			
	ln 23°C, 75 % RH		ln 23°C, 50 % RH - 60 % RH			
Al <sub>2</sub> O <sub>3</sub> layer thickness [nm]	0	50	0	25	50	100
Pigment-coated paper			>20000	>20000	>20000	>20000
LDPE coated paper	5,4	3,1				
PE (15 g/m <sup>2</sup> ) coated board	8,5	4,6	>20000	>20000	>20000	>20000
PLA (35 g/m <sup>2</sup> ) coated board	131	14	3150	49	121	513
PP film, 30 µm			1250	170	109	103
PET film, 50 µm			24	11	12	10
PLA film, 25 µm	93	3,3	315	44	32	57
PEN film, 25 µm	0,9	0,6				

Table 3.2. Water vapor and oxygen barrier with various structures [8].

WVTR [g/m <sup>2</sup> /day]				
In 23°C, 75 % RH				
Al <sub>2</sub> O <sub>3</sub> layer thickness [nm]	0	25	50	100
LDPE (15 g/m <sup>2</sup> ) coated board	7,0 ± 0,9	6,9 ± 0,1	2,0 ± 0,5	2,0 ± 0,5
PLA (35 g/m <sup>2</sup> ) coated board	64,9 ± 1,6	1,4 ± 0,2	1,8 ± 0,5	29,1 ± 5,1
OTR [cm <sup>3</sup> /m <sup>2</sup> /10 <sup>5</sup> Pa/day]				
In 23°C, 50 % RH - 60 % RH				
Al <sub>2</sub> O <sub>3</sub> layer thickness [nm]	0	25	50	100
LDPE (15 g/m <sup>2</sup> ) coated board	7900 ± 1600	6700 ± 2500	2700 ± 400	2300 ± 100
PLA (35 g/m <sup>2</sup> ) coated board	420 ± 10	20 ± 3	60 ± 3	200 ± 40

Table 3.3. Water vapor and oxygen barrier with various structures [9].

	WVTR [g/m <sup>2</sup> /day]	OTR [cm <sup>3</sup> /m <sup>2</sup> /10 <sup>5</sup> Pa/day]
	In 23°C, 75 % RH	In 23°C, 50 % RH - 60 % RH
a uncoated	65 ± 2	420 ± 10
a + Al <sub>2</sub> O <sub>3</sub> by H <sub>2</sub> O (100°C)	1 ± 0,2	20 ± 3
a + Al <sub>2</sub> O <sub>3</sub> by O <sub>3</sub> (100°C)	5 ± 2	12 ± 1
b uncoated	75 ± 2	400 ± 9
b + Al <sub>2</sub> O <sub>3</sub> by H <sub>2</sub> O (80°C)	3 ± 1	6 ± 1
b + Al <sub>2</sub> O <sub>3</sub> by O <sub>3</sub> (80°C)	7 ± 2	3 ± 1
b + Al <sub>2</sub> O <sub>3</sub> by O <sub>3</sub> (100°C)	1 ± 0,2	2 ± 0,2

a = PLA 35 g/m<sup>2</sup> + 310 g/m<sup>2</sup> coated board

b = PLA 35 g/m<sup>2</sup> + 210 g/m<sup>2</sup> coated board

Also temperature and handling of the samples have an influence of the barrier properties of the structure. Vähä-Nissi et al. have studied that there may be cracks in the ALD layer, because of e.g. straining after the ALD process. [10]

Surface energy of polymer can be increased by using corona pre-treatment before BALD coating. Terhi Hirvikorpi et al. found that OTR was improving but there wasn't remarkable effect on WVTR when Al<sub>2</sub>O<sub>3</sub> BALD coating was made after corona pre-treatment on PE surface. Concerning of PLA surface, the results aren't so clear, because deviation was increasing a lot with Al<sub>2</sub>O<sub>3</sub> BALD coating. [11]

### **3.2 Continuous ALD (CALD)**

In the continuous process the substrate is moving when precursors are attached onto the surface. Heating with microwave oven is a simple example of this. It is a batch process, if the tray stays still. It becomes a continuous process, if the tray starts to rotate. This continuous system is created for demonstrating the chemical bonding of molecules to a moving substrate.

CALD device, which has been used in this thesis, works a little bit differently than microwave system. The nozzles, through which the precursor gases are fed, are close to the coated surface and excess precursors are sucked away from the process between the nozzles. Thus, the inside surface of the ALD device won't be coated. Picture of this specific device is illustrated later in this thesis, in Figure 4.2.1.

### **3.3 Roll-to-Roll ALD (RRALD)**

Concerning the utilization of the ALD in packaging industry, the real target is the development of the RRALD device technology. The ALD device should be integrated to the rest of the line used for producing the packaging material.

Only a few RRALD devices have been made so far. There are big challenges how to utilize pressure and temperature low enough (heat-sensitive polymer) and how to prevent the precursor gases from mixing each other. An additional challenge is also to increase the speed of a substrate. In paper converting and laminating process, the typically speed of the substrate is few a hundreds of meters in a minute. Nowadays in RRALD, the web speed is only few meters in a minute.

One solution has already been used for research purpose in ASTRaL: a WCS 500 from Beneq presented in figure 3.1. It is likely the most suitable ALD device for paper converting industry for time being, because it can handle paper rolls which are exactly the same size and formula as they are after rewinding.



Figure 3.1. Roll-to-Roll ALD device WCS 500 by Beneq [12]

The WCS 500 can handle flexible roll-to-roll substrate materials. Maximum web width is 500 mm and maximum speed is 2 m/min. The maximum ALD process temperature is 150 °C. The device is built for industrial applications, such as many kinds of barriers to polymer based substrates and moisture barriers for flexible organic electronics and buffer layers for solar cells. [12] Solar cell manufacturing is a promising application area for RRALD in the future [13].

Unwinding and rewinding units are inside the WCS 500. It means that process pressure can be reduced to the required level from atmospheric pressure after the door is closed. Thus, web material travelling in and out from the low pressure chamber won't be a problem. Figure 3.2 shows the inside of WCS 500.

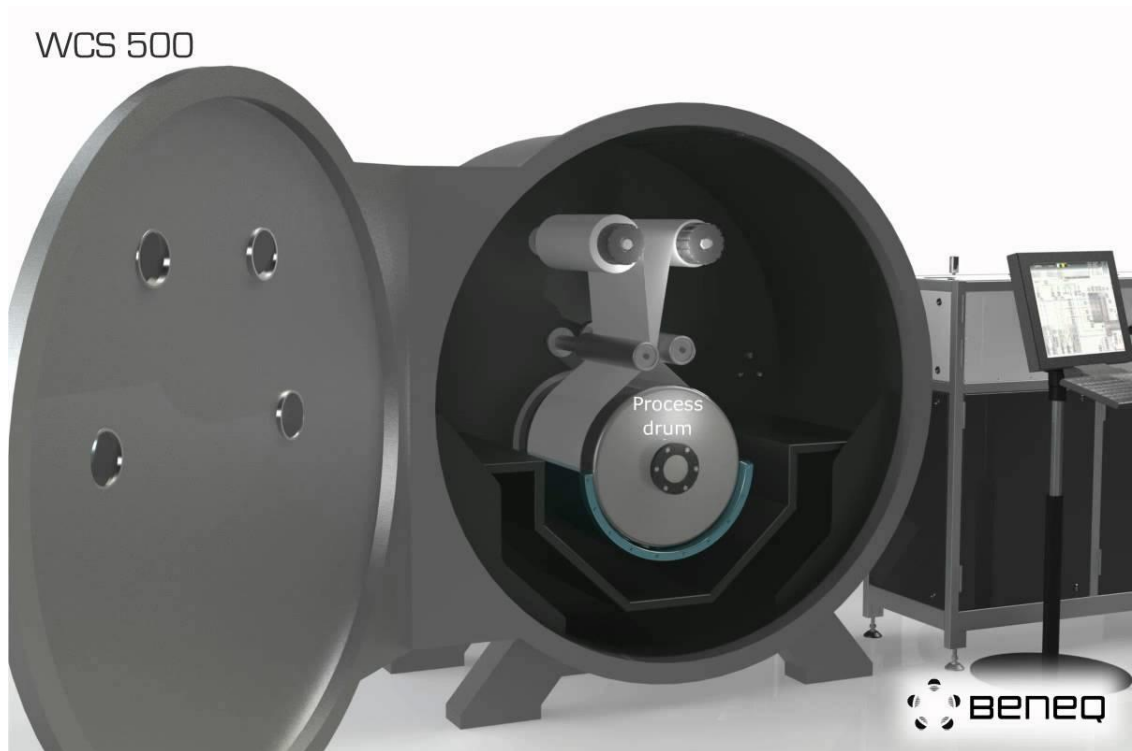


Figure 3.2. WCS 500 with open chamber [14]

In the upper left part is the unwinding and in upper right the rewinding. The web material wraps around the process drum. A coating head (blue) with multiple channels for the precursor and purge gases is moved back and forward along the web. The precursors are fed from this coating head and the ALD layer will grow only onto the outer surface of the web.

Nowadays narrow webs and low speeds are the main reasons, why the ALD is not yet used for packaging materials. Picosun Oy [15] and VTT have published some results made by Picosun's new RRALD coating device [16]. Other manufacturers, which are reporting about their activities with spatial or Roll-to-Roll ALD include e.g. SoLayTec/TNO [17, 18], Lotus [19], Kodak [20] and Levitec [21].

Nowadays many companies are developing RRALD devices working in lowered air pressure (not vacuum). Figure 3.3 shows how the gas flow is organized in an ALD device by Levitec.

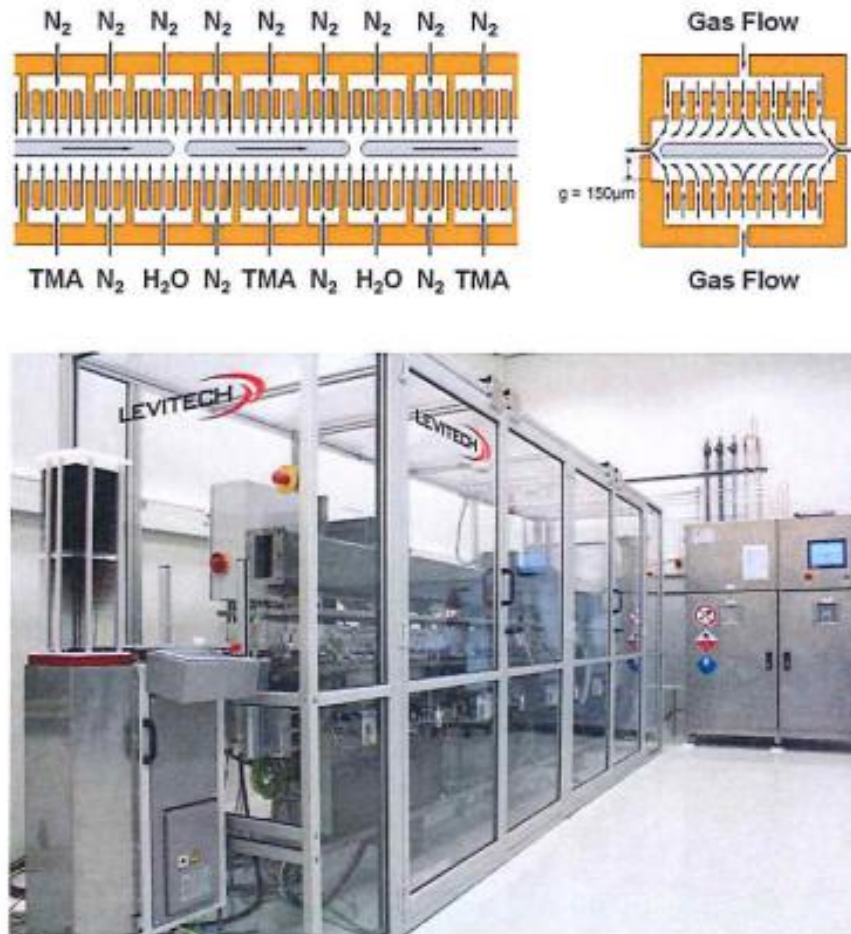


Figure 3.3. ALD device and gas flow in the process by Levitech [21]

In the upper figure 3.3, the  $N_2$  is required to ensure that TMA and  $H_2O$  would not react already in the gas phase. This kind of gas flow system in the ALD will encourage also other companies to start the development of their own solutions. Levitech is founded in 2009, so their technology is quite new. [21]



## 4 EQUIPMENT AND MATERIALS

In this thesis, all the activities were carried out in Paper Converting and Packaging Technology unit in Tampere University of Technology (TUT) or in Green Chemistry (previously ASTRaL, the name also used in this thesis) unit of Lappeenranta University of Technology (LUT), located in Mikkeli. Processes are divided into two different parts: Equipment: batch and continuous ALD, pilot line and finally laboratory analytics. Materials: first the ALD process in LUT and then extrusion coating process in TUT.

### 4.1 Equipment

This part of thesis contains all the essential information about the devices used for carrying out the necessary work in producing and analyzing the test samples. All work related to ALD coating has been done in LUT and other activities in TUT.

#### 4.1.1 BALD coating

In Mikkeli, ASTRaL unit has a batch ALD device TFS 500, which can be seen in figure 4.1.1. The device was manufactured by Beneq and it has been used in all BALD processes in this thesis. This is why this device is presented in more detail.



Figure 4.1.1. Thin Film System TFS 500 for ALD research and batch production [22]

The TFS 500 has been designed for diverse use in thin film coating applications. In this thesis all the material processed in the TFS 500 had two layers (paper or paperboard and polymer) and the polymer surface was ALD coated. This was the first Beneq reactor model. It has proved to be a versatile tool for both in-depth thin film research and robust batch processing. [22]

The TFS 500 can handle several types of substrates; wafers, planar objects, particles, porous bulk materials and 3D objects with high aspect ratio features. It can be equipped

with a manually operated load lock for increased wafer processing capabilities. Different types of reaction chambers can be fitted inside the vacuum chamber, which enables optimizing the reactor for different kind of applications. The TFS 500 meets both the requirements of industrial reliability and the need for flexibility of research and development operations. Process components are off-the-shelf articles and all precursor containers can be changed easily. [22]

The precursor readiness includes gases, liquids and solid materials. For a full flexibility in precursor selection, 500°C hot source option can be included. Table 4.1.1 includes more specific information about the batch ALD device in ASTRaL. [22]

Table 4.1.1. Technical specifications of TFS 500 [22].

Process temperature	25 - 500°C
Reaction chamber types and dimensions	-single wafer: $\varnothing 200 \times 3$ (mm), $\varnothing 300 \times 25$ (mm) -single wafer plasma: $\varnothing 200 \times 3$ (mm), $\varnothing 300 \times 3$ (mm) -3D/batch of wafers: $\varnothing 200 \times 170$ (mm) -3D/batch: $450 \times 300 \times 250$ (mm) -powder: $\varnothing 80 \times 50$ (mm) -solar cell batch: $156 \times 156$ (mm), 100 pcs
Gas lines	up to 5
Liquid sources (+5°C to ambient)	up to 4
Hot source HS 300 (ambient to 300°C)	up to 4
Hot source HS 500 (ambient to 500°C)	up to 2
Optional	- CCP plasma source (capacitively coupled) - manual load lock
Control system	PLC control with PC user interface
Main dimensions (L $\times$ W $\times$ H)	1600 $\times$ 900 $\times$ 1930 (mm)

The samples for the TFS 500 were sheet cut in TUT to the size of 13 cm x 13 cm, because this was the optimum sample size for the 3D reaction chamber with the current sample container. Typically the Al<sub>2</sub>O<sub>3</sub> ALD process in the TFS 500 will start with a 40 s ozone pulse followed by 90 s purge of nitrogen. Thereafter one deposition cycle consists of a 250 ms TMA pulse, 6 s purge, 3 s ozone pulse and 6 s purge.

#### 4.1.2 CALD coating

ASTRaL unit has a CALD device TFS 200R (figure 4.1.2). This device is also manufactured by Beneq and it was used in all the continuous ALD trials in this study.



Figure 4.1.2. Thin Film System TFS 200R for spatial ALD research [23]

The TFS 200R is the system designed for studying RRALD and other forms of continuous ALD. It is used exclusively for depositing thin films on flexible substrates. The TFS 200R enables investigation in the dynamic behavior of various precursor chemistries, simulation of process suitability and evaluation of film performance in RRALD applications. [23]

In the TFS 200R, the flexible substrate must be fixed on a rotating cylinder within the reaction chamber. The cylinder itself is surrounded by linear nozzles, each creating an isolated gas region over the full width of the substrate. As the cylinder is rotated, the substrate passes through different gas regions and gets coated. [23]

The TFS 200R is designed to meet both industrial standards and the flexibility requirements of research. Precursor containers are small, but they can be easily changed. Depending on the ALD process needs, the TFS 200R can be equipped with up to 2 heated sources (HS 80 and/or HS 180). The system can be equipped with up to 8 gas lines and up to 4 liquid sources. Table 4.1.2 shows more specific information about the CALD device in ASTRaL. [23]

Table 4.1.2 Technical specifications of TFS 200R [23].

Process temperature	25 - 200°C
Substrate size	up to 300 × 120 (mm)
Substrate material	polymer film, metal foil or anything flexible
Web speed	up to 300 m/min (@ 1000 rpm)
Process pressure	1 - 900 mbar (hPa)
Liquid sources, heated	up to 2
Liquid sources, not heated	up to 4
Gas lines	up to 8
Control system	PLC control with PC user interface
Main dimensions, ALD system (L × W × H)	1325 × 600 × 1298 (mm)
Main dimensions, electric cabinet (L × W × H)	1000 × 300 × 1600 (mm)

Typically the samples for TFS 200R tests were sheet cut in TUT to the size of 30 cm x 12 cm, because this is the maximum sample size for the rotating drum. The gas flow of precursors (TMA and water) and purge (nitrogen) were controlled with time and volume, because the sample was rotating continuously and it was passing each nozzle at the set speed.

### 4.1.3 Extrusion coating

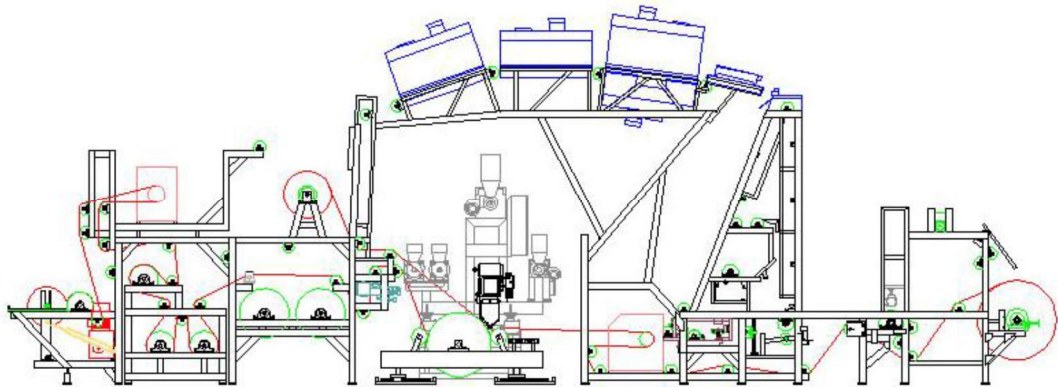


Figure 4.1.3. Paper Converting and Packaging Technology's pilot line in TUT [24].

Figure 4.1.3 shows the extrusion coating unit at the center and corona treatment next to it on the right side. Unwinding is at the very end on the right side. Immediately on the left side of the unwinding station is the flame treatment unit. Rewinding is at the end on the left side. General information, parameters and details, used at the trials in this thesis at TUT's pilot line are listed below [24]:

#### **Extrusion coating**

Four extruders, total output ~160 kg/h (LDPE).

All extruders (A, B, C and D) are equipped with hopper loader.

Max line speed 400 m/min.

Max web width 550 mm (recommendation 500 mm).

Laminating and cast film options.

#### **Main unwind**

Core 3" and 6"

Max web width 550 mm in extrusion.

Max roll diameter 1100 mm.

Roll materials: papers, board, etc.

#### **Rewind (Pope)**

Core 3" and 6"

#### **Extruder A**

Diameter 60 L/D, ratio 30 and max output ~90 kg/h (LDPE).

Moveable plastic melt temperature measurement unit

Pressure measurement unit

**Extruder B**

Diameter 40 L/D, ratio 24 and max output ~30 kg/h (LDPE).  
 Plastic melt temperature measurement unit  
 Pressure measurement unit

**Extruder C**

Diameter 30 L/D, ratio 25 and max output ~20 kg/h (LDPE).  
 Plastic melt temperature measurement unit  
 Pressure measurement unit

**Extruder D**

Diameter 30 L/D, ratio 25 and max output ~20 kg/h (LDPE).  
 Normally used for encapsulation

**Die**

Cloeren EBR™ III A  
 Internally deckled extrusion die  
 Lip heaters  
 Edge encapsulation system

**Feedblock**

Cloeren VG™ 5-Layer Dual Plane Feedblock  
 Streamline manifold

**2 different selector plugs**

(structure + encapsulation)  
 web--A-A-A-A-A---D/D  
 web--B-B-B-B-B---D/D

**Laminator**

Glossy or matt chill rolls  
 Chill roll diameter 800 mm and width 600 mm  
 Chill roll cooling or warming unit with temperature range 5 - 80 °C

**Corona (pre-treatment)**

Treatment power max 4kW  
 Ceramic electrodes

**Flame (pre-treatment)**

Max. heat output 50 kW  
 Gas supply propane

#### 4.1.4 WVTR

WVTR was measured with Aquatran (see details below). The gravimetric cup method (ASTM E96-10) was only used in the preliminary tests of this thesis. Here are details of Aquatran [25]:

##### **MOCON AQUATRAN MODEL 1G HIGH SENSITIVITY COULOMETRIC WATER VAPOR TRANSMISSION RATE TEST SYSTEM**

- Based on coulometric phosphorous pentoxide sensor
- WVTR range: 0,0005 – 5 g/m<sup>2</sup>/d (unmasked)
- Test temperature range: 10 – 40°C
- Relative humidity range: 35 – 90, 100 %
- DIN 53122:2

Figure 4.1.4 shows the Aquatran 1G in use at TUT's laboratory.



Figure 4.1.4. Aquatran 1G



#### 4.1.5 OTR

OTR was measured with Ox-Tran (see details below) [25]:

##### **MOCON OX-TRAN 2/21 MH and SS** STANDARD OXYGEN TRANSMISSION RATE TESTING SYSTEM

- Based on coulometric sensor
- O<sub>2</sub>TR range:
  - Unmasked: 0,05 – 200 cm<sup>3</sup>/m<sup>2</sup>/d
  - Masked: 0,5 – 2000 cm<sup>3</sup>/m<sup>2</sup>/d
- Test temperature range: 10 – 40 °C
- Relative humidity range: 0,35 – 90 %
- Edge leakage adaptors for coated papers/paperboards
- Package testing adaptors
- ASTM D3985 (films), ASTM F1927 (films), ASTM F1307 (packages)

Figure 4.1.5a shows the main oxygen barrier device (MH) and figure 4.1.5b the satellite device (SS), which can make measurements only at the atmospheric conditions 0 % RH.



Figure 4.1.5a. Ox-Tran 2/21 MH

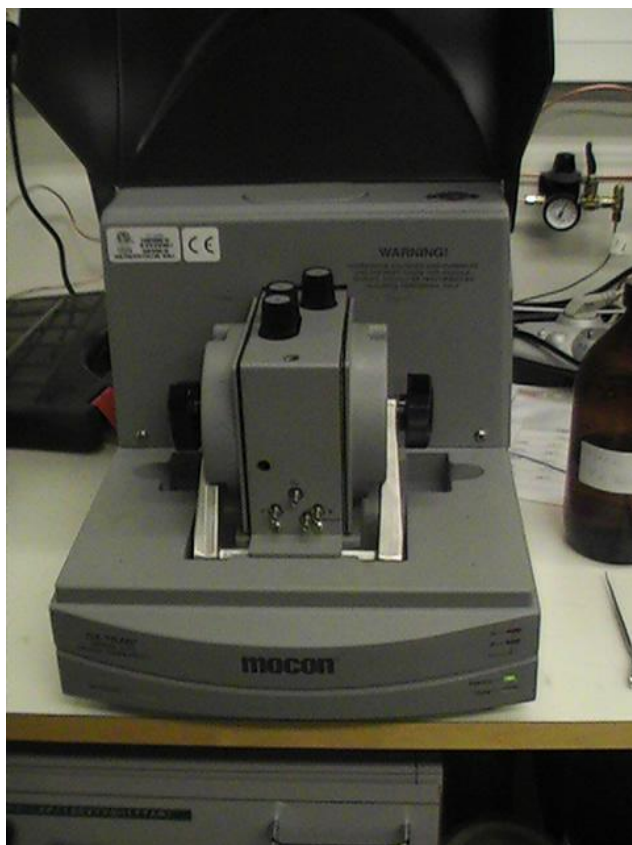


Figure 4.1.5b. Ox-Tran 2/21 SS

Both oxygen transmission devices locate in the laboratory of TUT and they are connected with the same gas (oxygen) lines. The samples are prepared exactly at the same way and measurements can be done simultaneously with both devices. Results in this thesis are made with both of these, but always only with the same OxTran when measuring samples from at specific trial.

#### 4.1.6 Adhesion

The peeling force was measured by Hounsfield H10KM. The force was measured from the structure (// shows the intended and realized place of peeling) of **paper-PET // PET or PLA or PE** and **paper-PET-ALD // PET or PLA or PE**. The Hounsfield is designed for testing e.g. plastics, metals, paper and adhesives and it can be seen in figure 4.1.6.

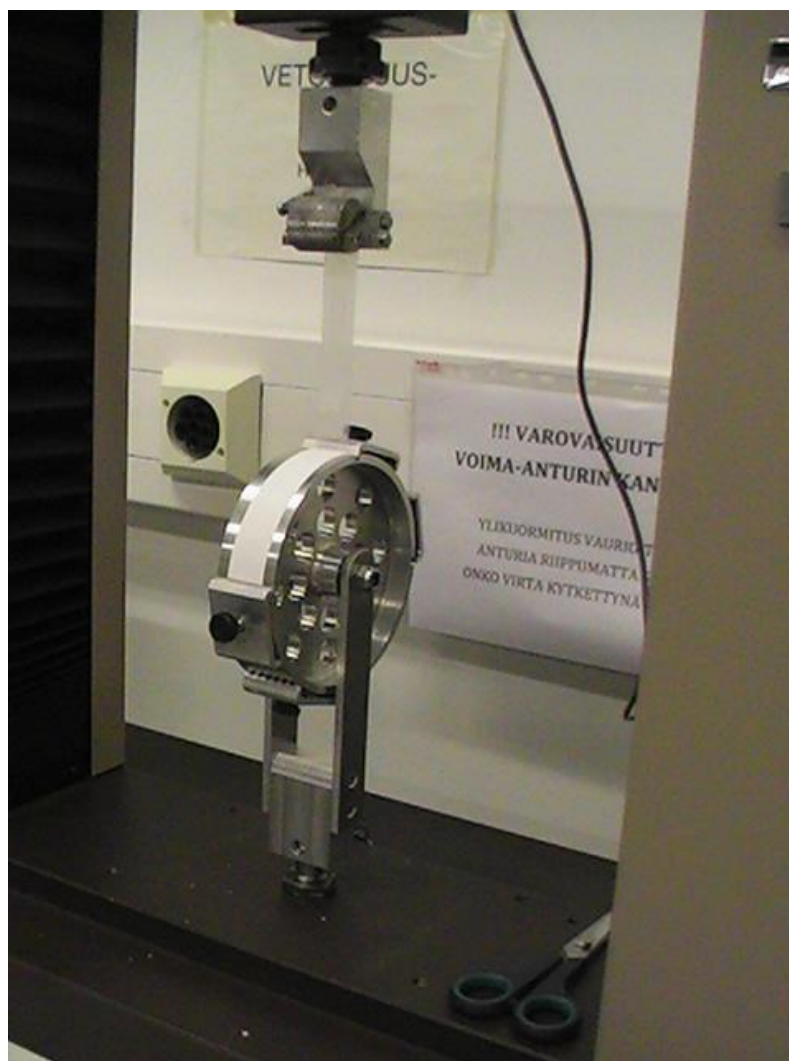


Figure 4.1.6. Sample peeling with Hounsfield.

Extrusion-coated polymers were separated from the base substrate by peeling the polymer layer at an angle of 90 degrees (L-peel test). All the samples had width of 14 mm and length of 130 mm. Sample was peeled for 20 mm, test speed was 40 mm/min and the peeling force was limited to 10 N. The used load cell was 100 N. The accuracy is guaranteed to within  $\pm 1\%$  of maximum force in accordance with BS160 A.S.T.M. E4. DIN 51221. [26]

The paper-PET(-ALD)-polymer -structure was attached to the rotating wheel from both ends. The top most extrusion coated layer was released at the other end and attached to the upper grip. The wheel had the same radial velocity as the grip. In consequence the peeling angle was always 90°. 4 or 5 parallel tests were carried out for each sample.

### 4.1.7 Surface energy

The contact angles were measured with water and ethylene glycol. The measurements were performed for PET and Al<sub>2</sub>O<sub>3</sub> ALD layer with a sessile drop method according to the standard ASTM-D 5946 [27]. The equipment used in the test was KSV CAM 200 (figure 4.1.7).

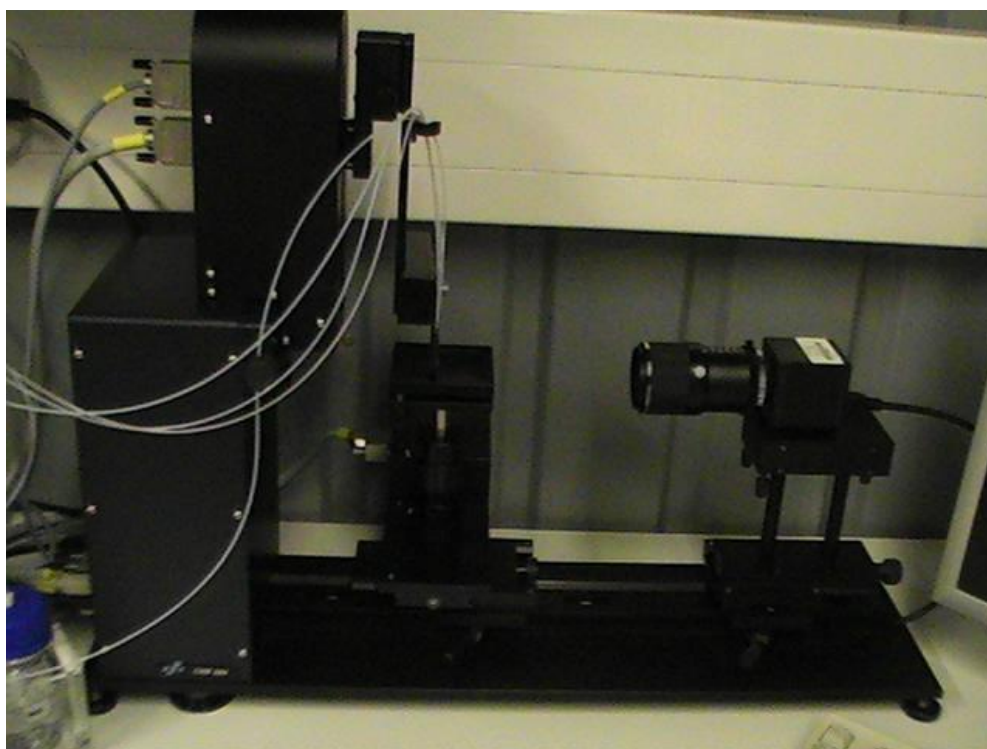


Figure 4.1.7. CAM 200 with ready to measure contact angle.

CAM 200 locates in the laboratory of TUT. Contact angles of water and ethylene glycol were recorded with a high-speed camera and converted to dispersive and polar components of surface energy. Six parallel measurements were made with both liquids.

## 4.2 Materials

Materials of these coating processes and trials have been divided into two different categories: ALD coating process and extrusion coating process. Every coated substrate for the ALD process had an extrusion coated polymer surface.

### 4.2.1 ALD coating

ALD processes in LUT can be divided into two categories: batch ALD (TFS 500) and continuous ALD (TFS 200R). Used materials were the same and the principle of creating the new atomic layer was the same. In  $\text{Al}_2\text{O}_3$  ALD process in TFS 500, the precursors were TMA (98 % purity by Volatec) and ozone (produced by ozone generator in ASTRAL) and in TFS200R, the precursors were TMA (98 % purity by Volatec) and deionized water. When using water as a precursor, the process temperature had to be at least  $100^\circ\text{C}$ . A purge gas was always nitrogen in both ALD coating processes.

Figure 4.2.1 shows the TFS 200R. The nozzles locate inside the chamber, from which the precursor and purge gases are fed to the process.



Figure 4.2.1. TFS 200R with opened lid [23]

The TMA is a liquid, when it is in a gas bottle. It gasifies, when the pressure is decreasing to the ALD process level.

### 4.2.2 Extrusion coating

In extrusion coating in TUT the main materials were polymer and fiber based substrate. The polymers were LDPE, PP, PLA and PET. The structure of the polymer coating in this thesis was always a mono extrusion coating and the coating thickness was high enough to avoid pinholes in coating.

Fiber based substrates in extrusion coating in TUT were paper and paperboard. Table 4.2.2 provides the main specifications for the base materials. The polymers were obtained from different manufacturers while the fiber based substrates were provided by Stora Enso as rolls of appropriate web length and width.

Table 4.2.2. Polymers and fiber based substrates used in trials in TUT.

Polymer	Name	Manufacture	$T_m$ [°C]	$T_g$ [°C]	
LDPE	CA7230	Borealis	109	-110	[2]
PP	WF420HMS	Borealis	163	-18	[2]
PLA	test grade		150-165	55-65	[28]
PET	Lighter C98	Equipolymers	247	78	[29]
<b>[g/m<sup>2</sup>]</b>					
Paper	Lumiflex	Stora Enso	80 or 90		[30]
Paperboard	Cupforma	Stora Enso	210		[31]

Both melting and glass-transition temperatures ( $T_m$  and  $T_g$ , respectively) of a polymer have to be note and taken into account, when planning of using the polymer as a substrate in the ALD process. If there is remarkable crystallization in the polymer under the ALD layer after the ALD process, this might lead to a cracking of the brittle ALD layer [32].

## 5 RESULTS

The results of this thesis have been divided into five different parts depending on the ALD process type or the test method used for analyzing the final samples. First part is BALD coating, second one is CALD coating and the next part is comparison between BALD and CALD. Fourth part deals with the surface energy of Al<sub>2</sub>O<sub>3</sub> ALD substrate and the final part covers adhesion of extrusion coating polymer to Al<sub>2</sub>O<sub>3</sub> ALD substrate.

### 5.1 BALD coating

It was assumed before the preliminary trials that the barrier properties would be improved with an Al<sub>2</sub>O<sub>3</sub> ALD layer. In the second phase the influence of ALD process parameters on the permeability of the final structure was studied. The final contains a comparison between the different extrusion coating polymers coated with an ALD layer. The main focus was on the permeability.

#### 5.1.1 Preliminary trials

When planning the very first paper/polymer/ALD trials, the main question was whether an ALD coating is really improving the water vapor and oxygen barrier of the LDPE extrusion coated paper. Nowadays, one reason for a thick polymer layer is a demand for good barrier properties of the package. It is possible to decrease the amount of polymer, if there is an extra ALD layer in the structure bringing very good barrier properties. Thus, when comparing the barrier properties of different structures, the thickness of the ALD layer must be constant, if the amount of LDPE on top of the paper will be changed. And of course the same thing with the other way around, if the amount of LDPE is constant, the thickness of ALD layer can be varied.

The amount of LDPE in extrusion coated products depends on the end use. In the case of CA7230 the coating weight cannot be under 7 g/m<sup>2</sup>, because of the material properties [33]. Extrusion coating trials in TUT were successful in producing samples of uniform quality for the ALD coating trials. The paper / LDPE –roll was cut to smaller pieces. Finally, a sheet cutter was used to cut the samples exactly to the size of 13 cm x 13 cm. This is the optimum size for a 2-dimensional sample for the TFS 500.

After the ALD trials with the TFS 500, the samples had the size of 10 cm x 10 cm containing ALD layer at the center of the sample. However, this surface area is perfect for the barrier tests where the measured area will be a circular 50 cm<sup>2</sup>. There is also enough area at the edges for gluing the sample between the aluminum foil masks for the Aquatran or OxTran.

The equipment, materials and parameters of extrusion coating, ALD process and laboratory analytics in the first trials were:

Extrusion coating: TUT pilot line, glossy chill roll

Base material: **Paper**, Lumiflex **90 g/m<sup>2</sup>**

Polymer: **LDPE**, CA7230. 3 coating weights: **18 g/m<sup>2</sup>**, **27 g/m<sup>2</sup>** and **36 g/m<sup>2</sup>**.

**Batch ALD** process: TFS 500, **65°C**

Precursors and layer: TMA and ozone, **Al<sub>2</sub>O<sub>3</sub>**

Cycles and time: TMA 0,25 s, purge 6 s, ozone 3 s and purge 6 s.

ALD layer: **10 nm** (120 cycles), **25 nm** (350 cycles) and **40 nm** (600 cycles)

Final Structure: Lumiflex / CA7230 / Al<sub>2</sub>O<sub>3</sub>

**WVTR**: Aquatran (DIN 53122:2) and cup method (SCAN P22:68),

**38°C**, **90 % RH**, **50 cm<sup>2</sup>**, 2 parallel samples

**OTR**: OxTran (ASTM D 3985),

**23°C** and **0 % RH**, **5 cm<sup>2</sup>**, 1 sample

The results of the barrier tests are presented in figures 5.1.1a, 5.1.1b and 5.1.1c.



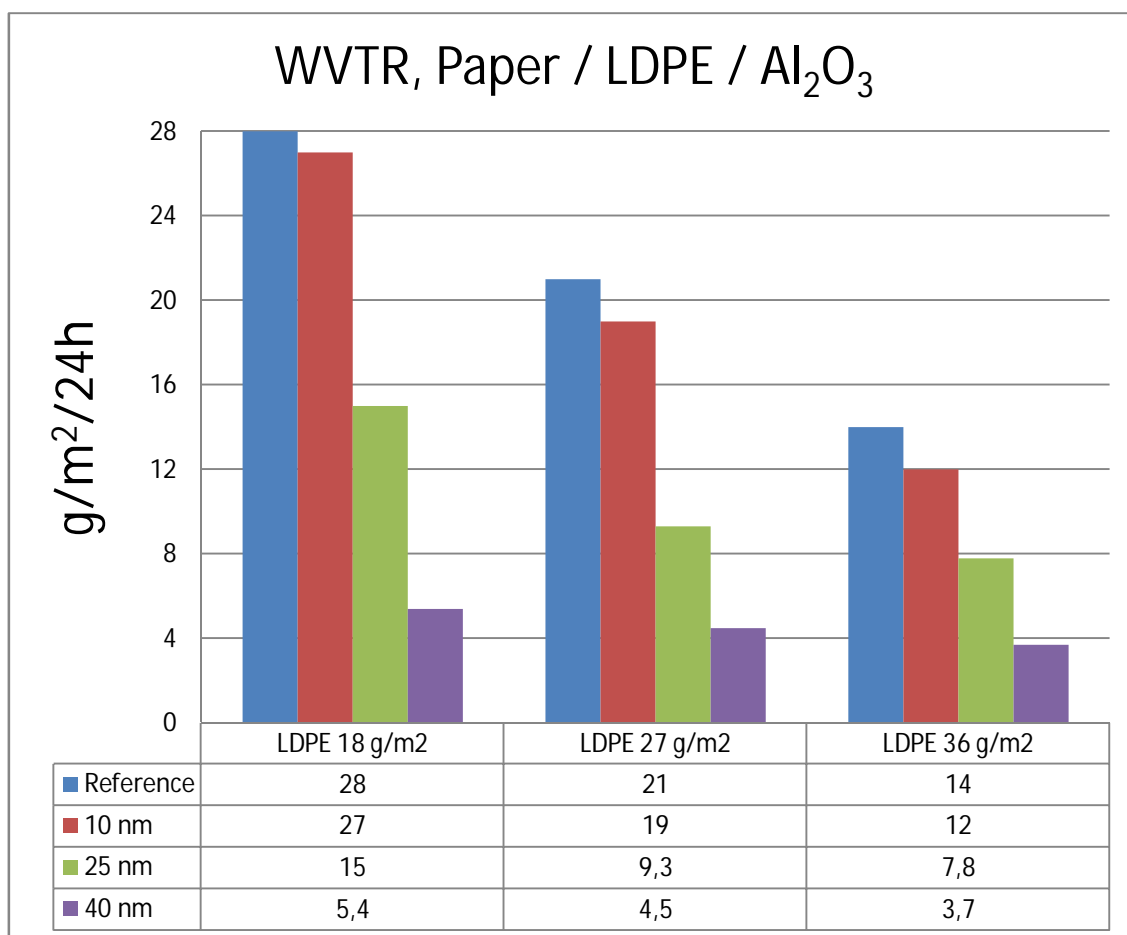


Figure 5.1.1a. WVTR (38°C, 90 % RH) of the Lumiflex / CA7230 / Al<sub>2</sub>O<sub>3</sub> -samples.

The results in figure 5.1.1a supported our assumption, that Al<sub>2</sub>O<sub>3</sub> ALD layer can improve the moisture barrier significantly. Increasing the thickness of the ALD layer led to improved barrier values. Figure 5.1.1b shows the same results in another graphical format.

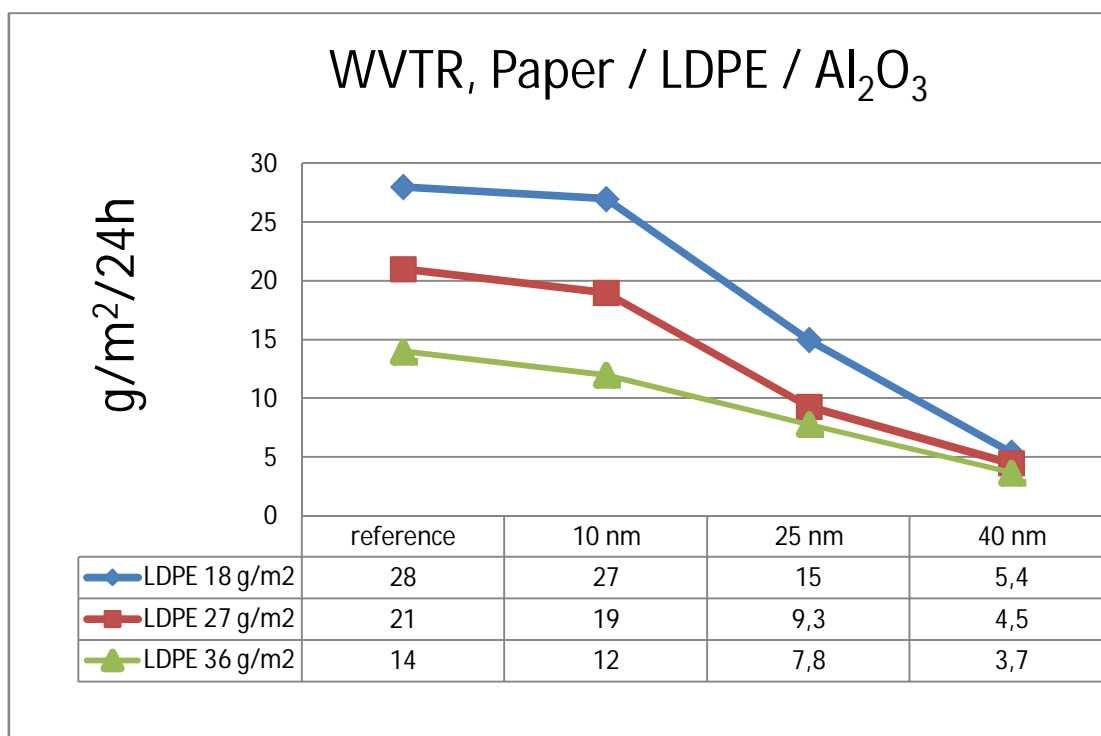


Figure 5.1.1b. WVTR (38°C, 90 % RH) of the Lumiflex / CA7230 / Al<sub>2</sub>O<sub>3</sub> -samples.

The thicker the ALD layer, the more it is dominating the total WVTR of the paper / LDPE / Al<sub>2</sub>O<sub>3</sub> ALD -structure. When comparing these WVTR results to the results for Hirvikorpi et al. (table 3.1 and 3.2) the values are about the same level, but there are also differences. Different materials, ALD process parameters and barrier test conditions make comparison between different studies difficult. It is difficult to know precisely how big an effect to the WVTR each parameter had compared to the total change in the WVTR. Materials and process parameters should be studied more in detail in future studies.

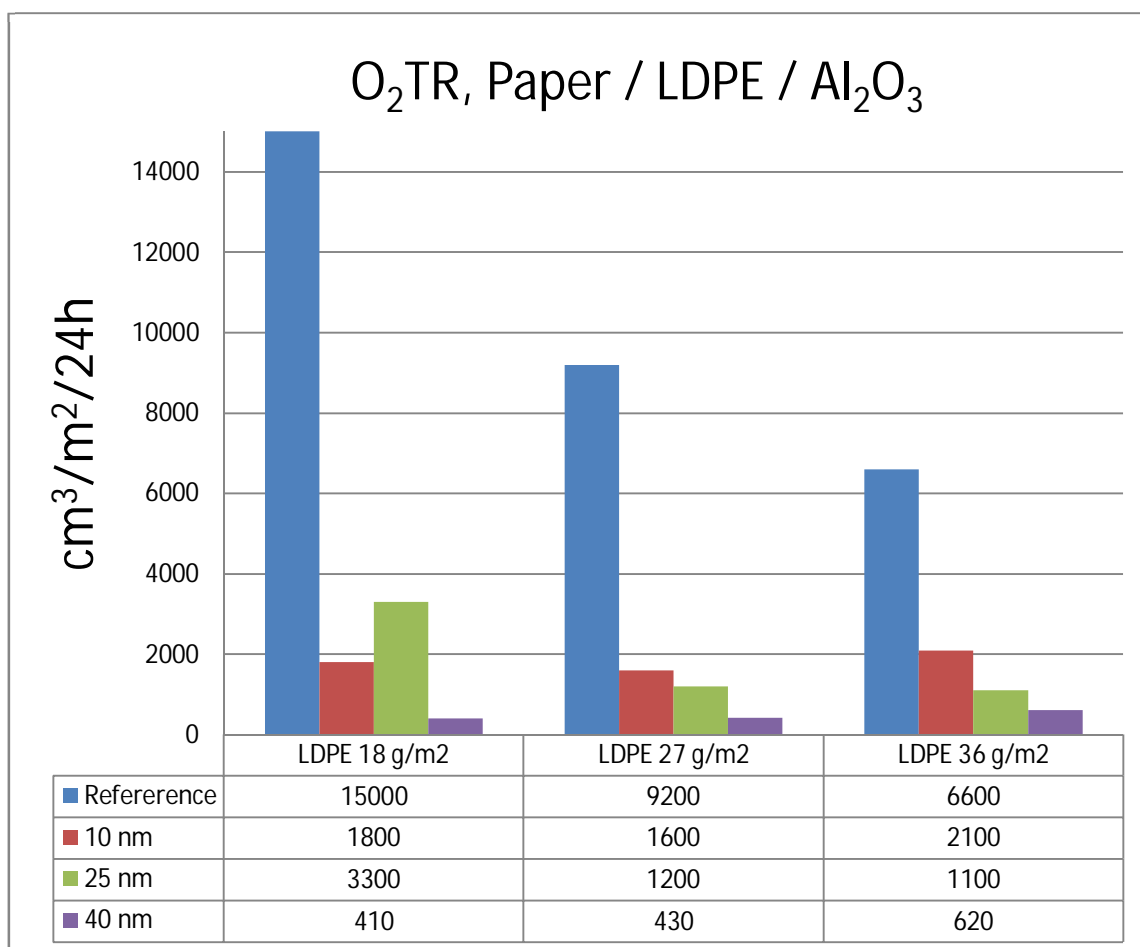


Figure 5.1.1c. OTR (23°C, 0 % RH) of the Lumiflex / CA7230 /  $Al_2O_3$  -samples.

The results in Figure 5.1.1c indicate that  $Al_2O_3$  ALD layer improved the oxygen barrier of the samples quite similarly to the moisture barrier. The amount of the LDPE and the thickness of the ALD layer together determine the oxygen barrier. However, when the thickness of  $Al_2O_3$  ALD layer was increased to 40 nm the ALD layer seemed to dominate the level of oxygen barrier. The thickness of the LDPE layer under the ALD layer became insignificant when comparing the oxygen barrier results. Hence, the amount of the LDPE coating can be decreased without sacrificing the oxygen barrier of the ALD coating.

The thickness of  $Al_2O_3$  ALD layer might not be precisely constant between parallel samples, because the samples were placed to different locations in the chamber of TFS 500 in the ALD process. Thus, there can be deviation in barrier properties of samples having different amount of polymer, because there can be different thickness of  $Al_2O_3$  ALD layer on top of the polymer and thick ALD layer seemed to dominate the level of oxygen barrier.

### 5.1.2 Influence of ALD process parameters on permeability

After the first paper/polymer/ALD trials, the target was to compare different materials and process parameters. In the following trials various substrates and extrusion coatings were used with ALD coating and their effect on barrier was studied.

It would be interesting to change the oxidizing precursor from ozone to water, because an Al<sub>2</sub>O<sub>3</sub> ALD layer can also be created with TMA and water. Increasing the deposition temperature from 65°C to 100°C could lead to different barrier performance. Now the precursor was ozone in both cases and the only variable was the process temperature.

Extrusion coating trials were successful and homogenous paper / LDPE and paper / PP rolls were produced. Again, the samples were cut to the size of 13 cm x 13 cm. The samples were then sent to the ALD trials (TFS 500). However, this time two different reaction temperatures (65°C and 100°C) and two different oxidizing precursors (water and ozone) were used with TMA.

The equipment, materials and parameters of extrusion coating, ALD process and laboratory analytics in the second trials were:

Extrusion coating: TUT pilot line, glossy chill roll  
 Base material: Paper, Lumiflex 90 g/m<sup>2</sup>  
 Polymer: **PE** CA7230 or **PP** WF420HMS. Both coating weight of 30 g/m<sup>2</sup>

Batch ALD process: TFS 500, **65°C or 100°C**  
 Precursors and layer: TMA and **ozone or water**, Al<sub>2</sub>O<sub>3</sub>  
 ALD layer: **1660 cycles, 1200 cycles or 1000 cycles**

Final Structure: Lumiflex / CA7230 / Al<sub>2</sub>O<sub>3</sub> or Lumiflex / WF420HMS / Al<sub>2</sub>O<sub>3</sub>

**WVTR:** Aquatran **23°C, 50 % RH and 38°C, 90 % RH**  
 50 cm<sup>2</sup>, 2 parallel samples

**OTR:** OxTran, **23°C and 0 % RH**  
 5 cm<sup>2</sup>, 1 sample

The barrier results are presented in figures 5.1.2 and 5.1.3. Both tests were carried out with exactly the same samples. First the sample was tested for the WVTR in normal conditions (23°C, 50 % RH) followed by test in tropical conditions (38°C, 90 % RH).

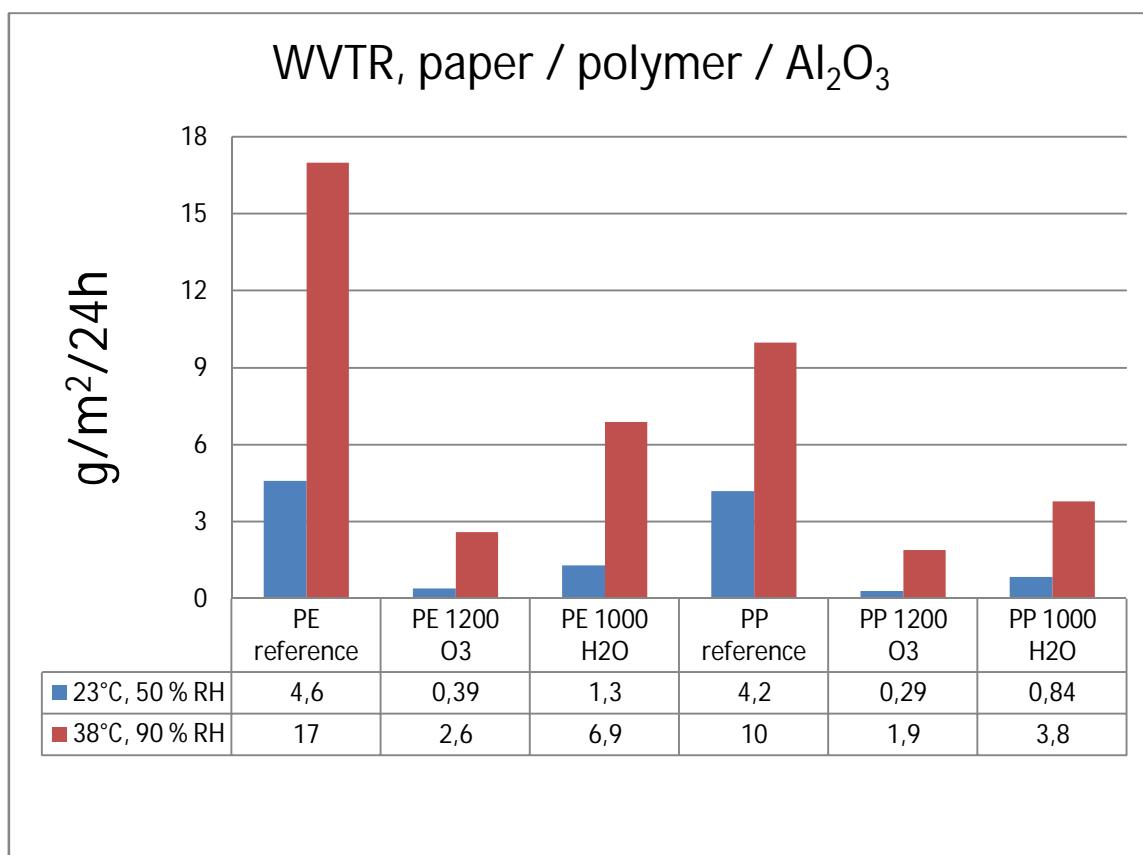


Figure 5.1.2. WVTR results with two different polyolefins and two different oxidizing precursors.

The results in figure 5.1.2 show that PP was a little bit better moisture barrier than LDPE with and without the ALD layer. Ozone might have been a better precursor than water with TMA, but this couldn't be proved as the number of the ALD cycles and the ALD process temperature were not the same. As expected, values are lower in normal conditions than in tropical conditions. Both polyolefins coated with an Al<sub>2</sub>O<sub>3</sub> ALD layer provided approximately 10 times better water vapor barrier than the references without the ALD layer.

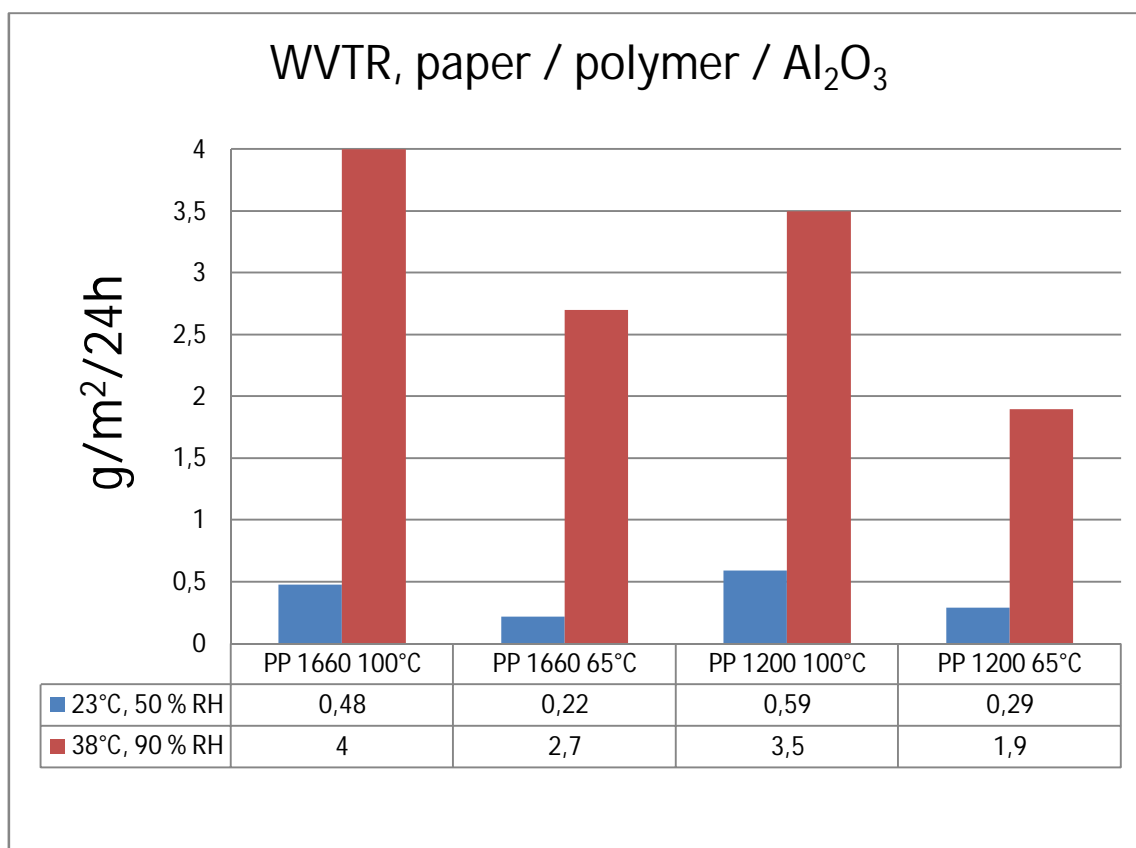


Figure 5.1.3. Comparison of WVTR values with two different ALD process temperatures.

The ALD process temperature of 65°C gave a slightly better moisture barrier than 100°C with the TMA + ozone process on PP coated substrate. Roughly the same values were achieved with both 1660 cycles and 1200 cycles. This assumption advises to use 65°C with the TMA + ozone process, if the target is to achieve as good moisture barrier as possible.

The growth rate of an ALD layer in the process in both temperatures (65°C and 100°C) is unknown. Thus, it is difficult to find out the reason of different WVTR between the samples, because the thickness and density of the Al<sub>2</sub>O<sub>3</sub> ALD layer may be different after the same amount of cycles.

### 5.1.3 Influence of extrusion coating polymer to permeability

After studying polyolefins coated with ALD layer, the idea of using polyester and biopolymers emerged. Polyethylene terephthalate (PET) is a strong polymer and it can tolerate higher temperatures than many other polymers. PET is used in many barrier products also because it is insensitive to many solvents. [34] Nowadays it is possible to manufacture PET partly from renewable sources [35]. In addition, the first 100 % recycled soda bottle by Pepsi was launched 2011 [36].

Poly(lactic acid) (PLA) biopolymer was chosen to be studied in this thesis, because it is the most important bioplastic nowadays [37]. PLA is used today in different kinds of solutions in medical, packaging and other commercial applications and its capability to replace polyolefins is being studied intensively [38]. PLA is also commercially widely available.

Extrusion coating trials with PET were challenging, because the target was to produce about a 25 g/m<sup>2</sup> coating layer of PET on top of the paper. This was not easy because of the poor adhesion properties of PET. After a few trials we succeeded to have a PET coating of roughly 27 g/m<sup>2</sup> with a fair adhesion to paper. The samples were cut again to the size of 13 cm x 13 cm and sent to the ALD trials (TFS 500). The parameters in these ALD trials were the number of cycles and the process temperature.

The equipment, materials and parameters of extrusion coating, ALD process and laboratory analytics in the third trials were:

Extrusion coating: TUT pilot line, glossy chill roll

Base material: Paper, Lumiflex 90 g/m<sup>2</sup>

Polymers: **PET** S98 coating weight of 27 g/m<sup>2</sup>; **PLA** coating weight of 25 g/m<sup>2</sup>; **PE** CA7230; **PP** WF420HMS, both coating weight of 30 g/m<sup>2</sup>

Batch ALD process: TFS 500, **65°C or 150°C**

Precursors and layer: TMA and **ozone**, Al<sub>2</sub>O<sub>3</sub>

ALD layer: **600 cycles, 1200 cycles or 1660 cycles**

The thickness of Al<sub>2</sub>O<sub>3</sub> ALD layer was also measured at the surface of silicon wafer after the ALD process, because there were thickness deviations between different temperatures of the ALD processes.

Final Structure: Lumiflex / PET or PLA or PE or PP / Al<sub>2</sub>O<sub>3</sub>

**WVTR:** Aquatran **23°C, 50 % RH and 38°C, 90 % RH**

50 cm<sup>2</sup>, 2 parallel samples

**OTR:** OxTran, **23°C and 0 % RH**

5 cm<sup>2</sup>, 2 parallel samples

The results from the water vapor permeability measurements are presented in figures 5.1.4 and 5.1.5. Blue color in the figure represents the permeability values in normal conditions (23°C, 50 % RH) followed by the test results from exactly the same samples in tropical conditions (38°C, 90 % RH) in red.

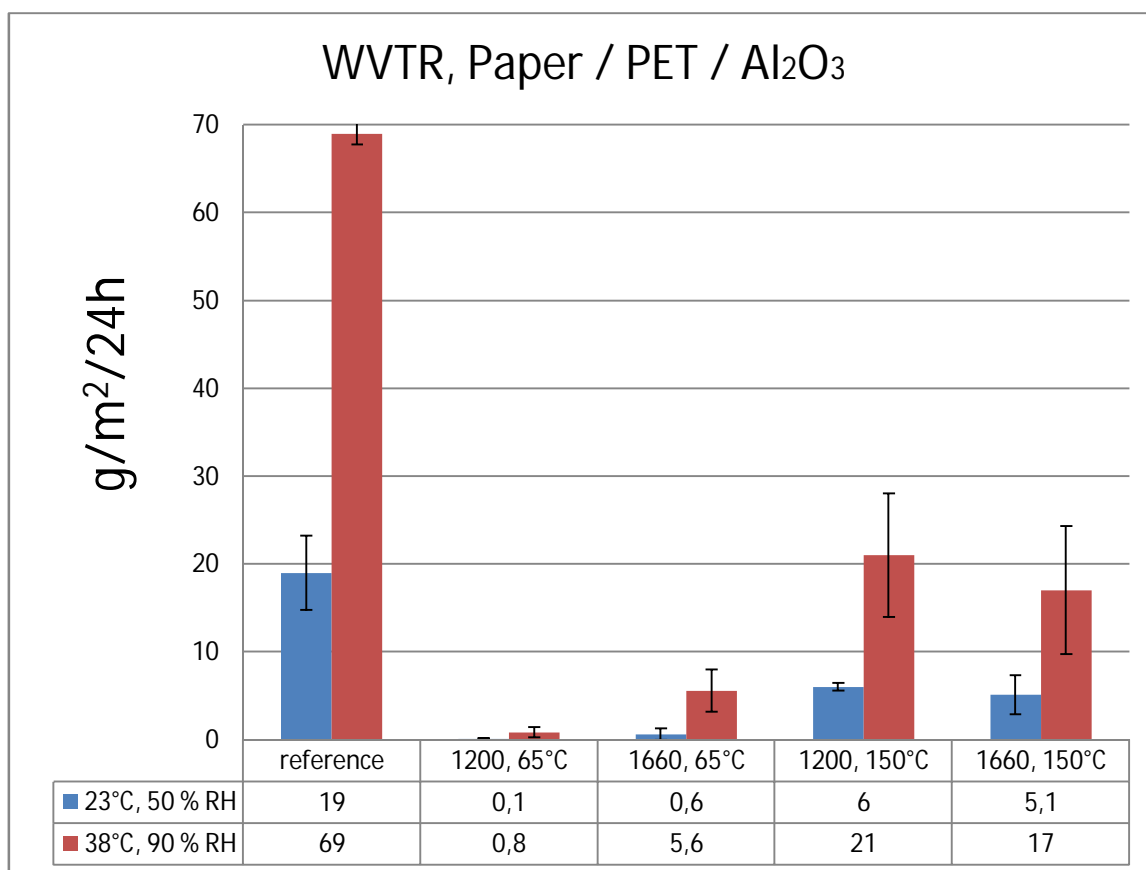


Figure 5.1.4. Influence of ALD process temperatures and number of ALD cycles on water vapor permeability of PET coated paper.

The measured thicknesses of the ALD layers on top of the silicon wafers were:

**120 nm (1200 cycles, 65°C)**

**190 nm (1660 cycles, 65°C)**

**80 nm (1200 cycles, 150°C)**

**90 nm (1660 cycles, 150°C)**

The thickness of ALD layer was much higher, when the ALD process temperature was 65°C compared to that of 150°C. The density of the Al<sub>2</sub>O<sub>3</sub> ALD layer wasn't measured from the silicon wafers.

150°C was too high ALD process temperature when the target was to achieve as good moisture barrier as possible. In the previous trials it was shown that in 65°C provided better barrier than 100°C. Thus, 65°C is likely a better process temperature than 100°C or higher. There was a remarkable improvement in the moisture barrier when comparing the samples with the ALD layer (process temperature 65°C) to the reference, the WVTR value is approximately 100 times better. PET seems to be a very good substrate for the Al<sub>2</sub>O<sub>3</sub> ALD layer.



Increasing the number of cycles from 1200 to 1660 didn't show any improvement in the moisture barrier but the deviation in the test results grew a lot. Similarly to the previous trials, there is no reason to increase the number of ALD cycles above 1200 when the target is to achieve as good moisture barrier as possible to the structure.

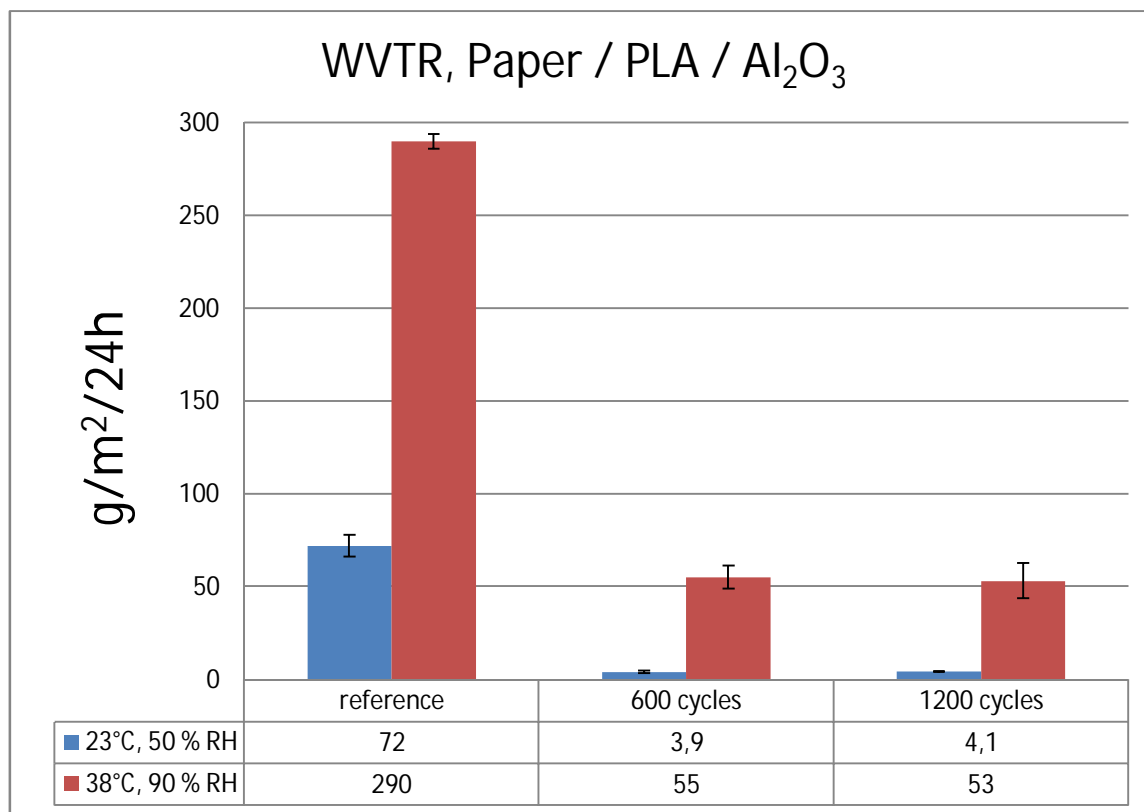


Figure 5.1.5. WVTR of PLA coated paper with two different numbers of cycles (ALD process temperature 65°C)

The measured thicknesses of the ALD layers on top of the silicon wafers were:

**65 nm (600 cycles)**

**110 nm (1200 cycles)**

According to results in figure 5.1.5 it seemed that the improvement with PLA coated paper was higher in normal than in tropical conditions. On the other hand, with PET and polyolefins this kind of difference was not as clear. Increasing the amount of cycles from 600 to 1200 didn't show any improvement in measured moisture barrier of the PLA / Al<sub>2</sub>O<sub>3</sub> -structure.

The figures 5.1.6 and 5.1.7 present the oxygen barrier results for the PET coated paper. The test conditions were 23°C, 0 % RH. The samples in figure 5.1.6 are the same as those used in figure 5.1.4.

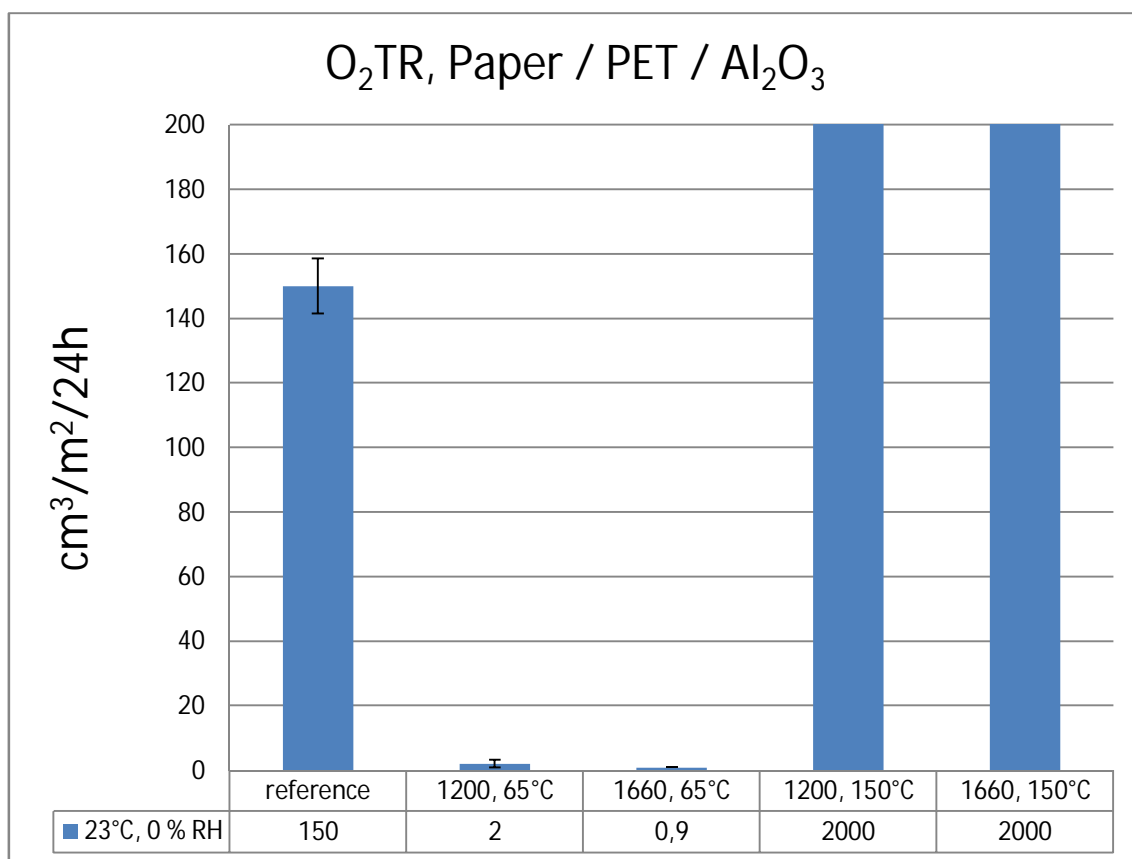


Figure 5.1.6. Influence of ALD process temperatures and number of cycles on the oxygen permeability of PET coated paper.

The measured thicknesses of the ALD layers on top of the silicon wafers were:

**120 nm (1200 cycles, 65°C)**

**190 nm (1660 cycles, 65°C)**

**80 nm (1200 cycles, 150°C)**

**90 nm (1660 cycles, 150°C)**

Oxygen barrier at 65°C is amazingly good when  $Al_2O_3$  ALD layer is on top of the PET, like in the case of the water vapor barrier. The oxygen barrier is about 100 times better than the PET coated paper without the ALD layer. The barrier was improved only slightly when the number of cycles was increased from 1200 to 1660.

The ALD process temperature of 150°C weakened the oxygen barrier of the structure. The oxygen permeation rate values in 150°C were higher than the reference values. Thus, the ALD process temperature of 150°C made the PET substrate a poorer oxygen barrier than what it was before the ALD. The scale of the figure 5.1.6 is only up to 200 (cm<sup>3</sup>/m<sup>2</sup>/24h). The results in 150°C were over 2000 (cm<sup>3</sup>/m<sup>2</sup>/24h), which was the maximum limit of the OxTran test device value.

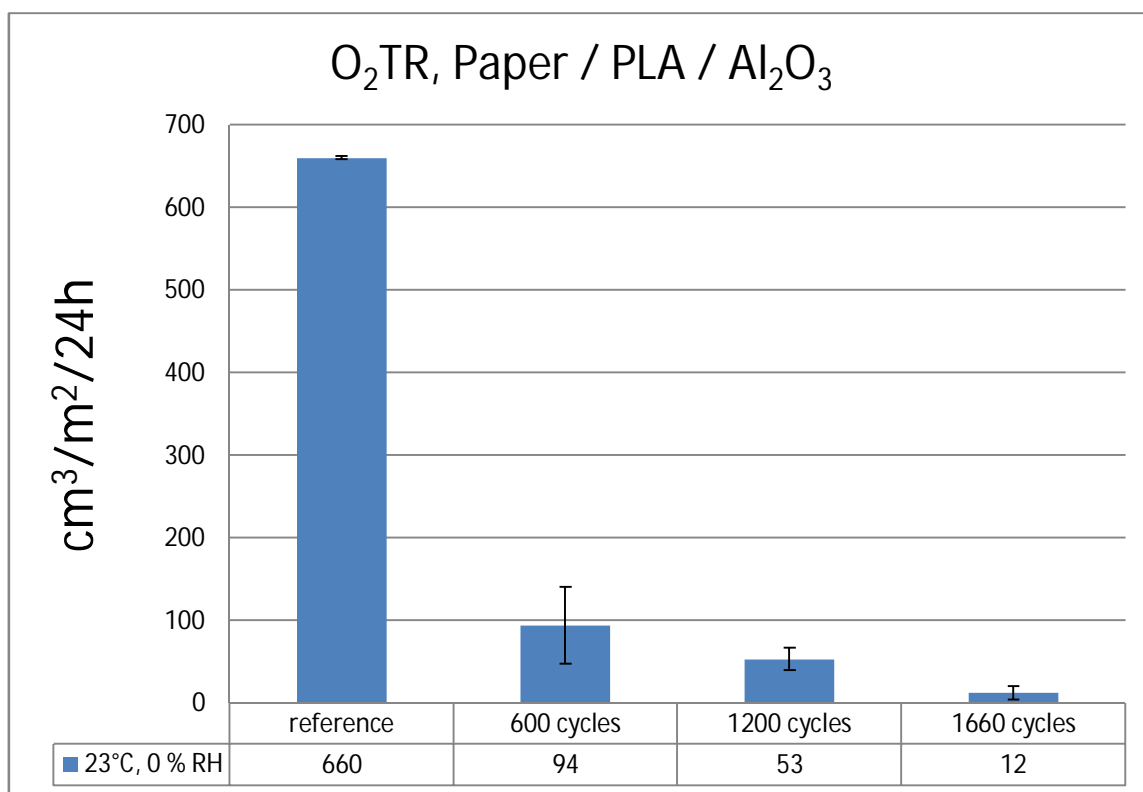


Figure 5.1.7. OTR of PLA coated paper after different number of cycles (ALD process temperature 65°C)

The measured thicknesses of the ALD layer on top of the silicon wafers were:

- 65 nm (600 cycles)**
- 110 nm (1200 cycles)**
- 200 nm (1660 cycles)**

PLA coated paper with an  $Al_2O_3$  ALD layer has from 7 to 55 time lower oxygen permeability than the reference. PLA coating as such is not as good oxygen barrier as PET. The OTR values with  $Al_2O_3$  ALD layer were also clearly higher on top of the PLA than on top of the PET when comparing figures 5.1.6 and 5.1.7.

The oxygen barrier was improved with a higher number of ALD cycles. This improvement was relatively more pronounced with PLA than with PET when comparing figures 5.1.6 and 5.1.7.

When the target is to achieve an excellent water vapor barrier with PET or PLA there is no need to go for thick  $Al_2O_3$  ALD layers. The oxygen barrier, however, is improving with an increasing number of ALD cycles. The temperature of the ALD process should be rather 65°C than 150°C as far as improved barrier is concerned.

When comparing the WVTR and OTR results with PLA structures to those from Hirvikorpi et al. (tables 3.1, 3.2 and 3.3), the values are approximately at the same level in the case of WVTR. The different materials and ALD process parameters are, however, affecting so strongly to the results that direct comparison is difficult, but a huge improvement can be seen with the ALD in the studies. A continuous improvement in the OTR with an increasing thickness of Al<sub>2</sub>O<sub>3</sub> ALD layer was observed in this study. Hirvikorpi et al. typically found an optimum thickness above which the OTR increased.

Figures 5.1.8 and 5.1.9 present the results of the moisture and oxygen permeability measurements. The precursors were TMA and ozone, the number of cycles was 1200 and the ALD process temperature was 65°C.

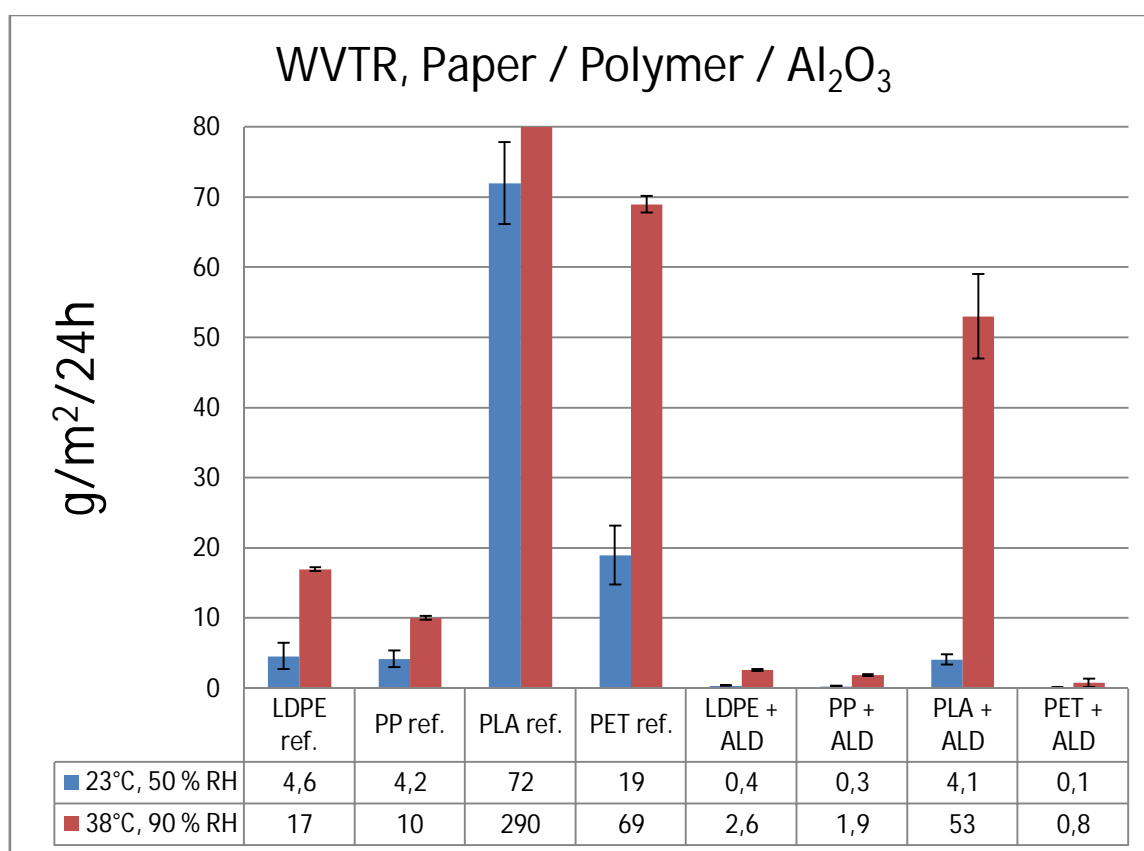


Figure 5.1.8. Comparison of WVTRs of polymers with and without a BALD layer.

There was a huge difference between the reference values in figure 5.1.8, and the y axis had to be adjusted accordingly. The value of PLA (290 g/m<sup>2</sup>/24h) in tropical conditions is much higher than the maximum value on the y axis.

The moisture permeation of polymers with an Al<sub>2</sub>O<sub>3</sub> ALD layer was at a much lower level compared to the references. The relative improvement in the permeability values are compared in table 5.1.1. The WVTR values of a polymer have been divided by the WVTR values of the polymer with an ALD layer in normal and tropical conditions.

Table 5.1.1. Relative improvements in the WVTR of the polymers with an Al<sub>2</sub>O<sub>3</sub> ALD layer.

	$\frac{\text{WVTR (polymer)}}{\text{WVTR (polymer + Al}_2\text{O}_3 \text{ ALD)}}$			
	LDPE	PP	PLA	PET
23°C, 50 % RH	12	14	18	190
38°C, 90 % RH	6,5	5,3	5,5	86

Al<sub>2</sub>O<sub>3</sub> ALD layer on PET brings a significant improvement in the WVTR compared to the PET reference. WVTRs of LDPE, PP and PLA were improved with an Al<sub>2</sub>O<sub>3</sub> ALD layer to 12 - 18 times lower values in normal conditions. In tropical conditions the improvement was somewhat lower than in normal conditions with all the polymers.

The total permeability of a multilayer polymer laminate can be calculated using the following equation. Densities and entropies of polymers are assumed constant [39].

$$\frac{1}{\bar{P}} = \frac{x_1}{P_1} + \frac{x_2}{P_2} \dots \dots \dots + \frac{x_n}{P_n}$$

n = number of a layer

x = thickness of a layer

P = permeability

The Al<sub>2</sub>O<sub>3</sub> ALD layer is not suitable for this equation, because its thickness cannot be determined accurately and the layer has to be definitely pinhole free. Thus, a statistical model suggested by Lahtinen [4] cannot be used as a predictive tool for calculating the WVTR of the Al<sub>2</sub>O<sub>3</sub> ALD layer alone.

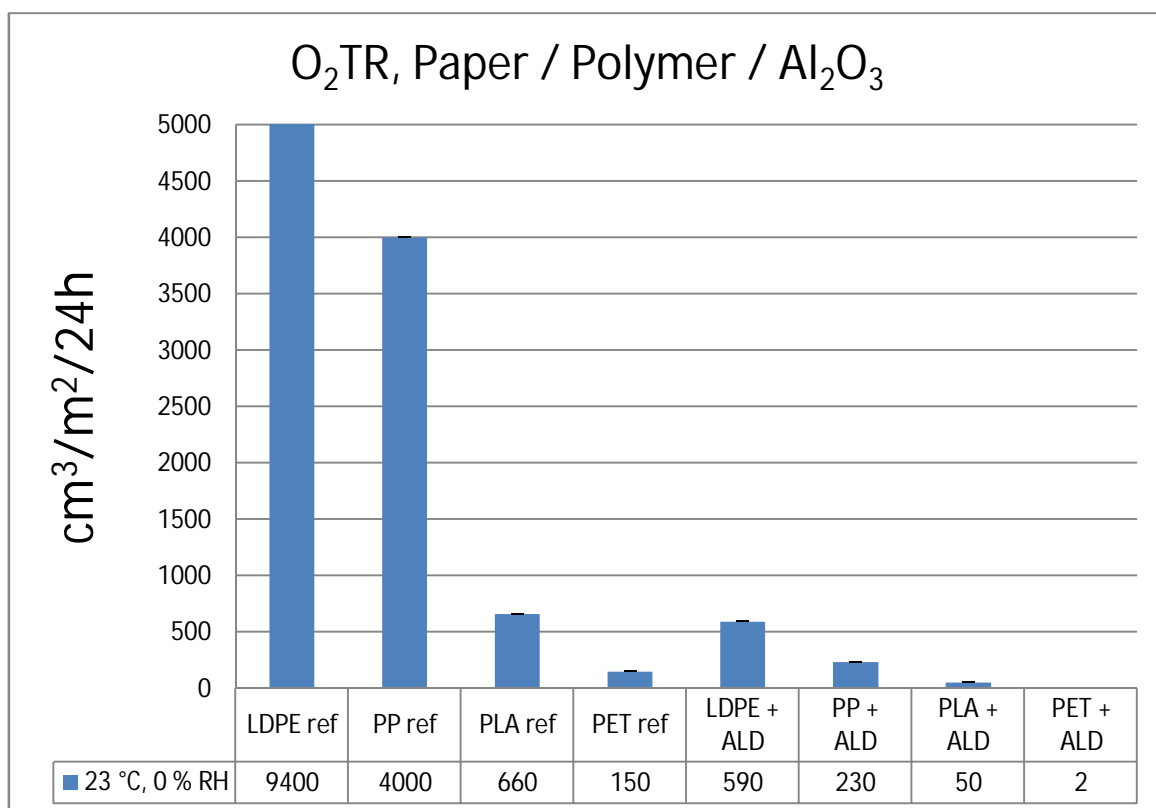


Figure 5.1.9. Comparison of OTRs of polymers with and without a BALD layer.

Figure 5.1.9 shows that there were significant differences between the reference values, and the y axis had to be adjusted accordingly. The value of LDPE reference (9400  $cm^3/m^2/24h$ ) is higher than the maximum value on the y axis.

Table 5.1.2 presents the measured OTR values of polymers divided by the measured OTR values of polymers with an ALD layer in dry conditions.

Table 5.1.2. Relative improvement in the OTR with an  $Al_2O_3$  ALD layer.

$$\frac{OTR(\text{polymer})}{OTR(\text{polymer} + Al_2O_3 \text{ ALD})}$$

	LDPE	PP	PLA	PET
23°C, 0 % RH	16	17	13	75

There is an enormous improvement in the OTR of PET by the  $Al_2O_3$  ALD layer. OTRs of LDPE, PP and PLA were improved with an  $Al_2O_3$  ALD layer to 13 - 17 times lower values. PET seems to be the best of these polymer surfaces for an  $Al_2O_3$  ALD layer, when the target is to achieve as good moisture and oxygen barrier as possible. LDPE, PP and PLA are about at the same level when the relative improvements in the WVTR and OTR are compared.

## 5.2 CALD coating

After studying ALD coating with stationary polymer surfaces, the next obvious step towards Roll-to-Roll ALD process is to extend the ALD process to moving substrates. The idea was to study if this concept works and if it can be controlled in the same as the batch ALD process.

The substrates and test structures in these trials were exactly the same as in the previous trials. The references were also the same. This time the samples were cut to a size of 12 cm x 30 cm and sent for continuous ALD trials with the TFS 200R. In the CALD process the samples were taped against a cylinder, and the deposition process takes place on the outer surface of the taped samples.

The equipment, materials and parameters of extrusion coating, ALD process and laboratory analytics in the fourth trials (and first CALD trials) were:

Extrusion coating: TUT pilot line, glossy chill roll

Base material: Paper, Lumiflex 90 g/m<sup>2</sup>

Polymers: **PET** S98, coating weight of 27 g/m<sup>2</sup>, **PLA** coating weight of 25 g/m<sup>2</sup>, **PE** CA7230 and **PP** WF420HMS, both coating weight of 30 g/m<sup>2</sup>

Continuous ALD process: TFS 200R, **100°C**

Precursors and layer: TMA and **water**, Al<sub>2</sub>O<sub>3</sub>

ALD layer: **1000 cycles**

Final Structure: Lumiflex / PET or PLA or PE or PP / Al<sub>2</sub>O<sub>3</sub>

**WVTR:** Aquatran **23°C, 50 % RH and 38°C, 90 % RH**

50 cm<sup>2</sup>, 2 parallel samples

**OTR:** OxTran, **23°C and 0 % RH**

5 cm<sup>2</sup>, 2 parallel samples

The results from the moisture permeability measurements are presented in figure 5.2.1. The reference values are the same as in figure 5.1.8. Blue color indicates the test was carried out in normal conditions (23°C, 50 % RH) and red color is used for the results obtained from exactly the same samples in tropical conditions (38°C, 90 % RH).

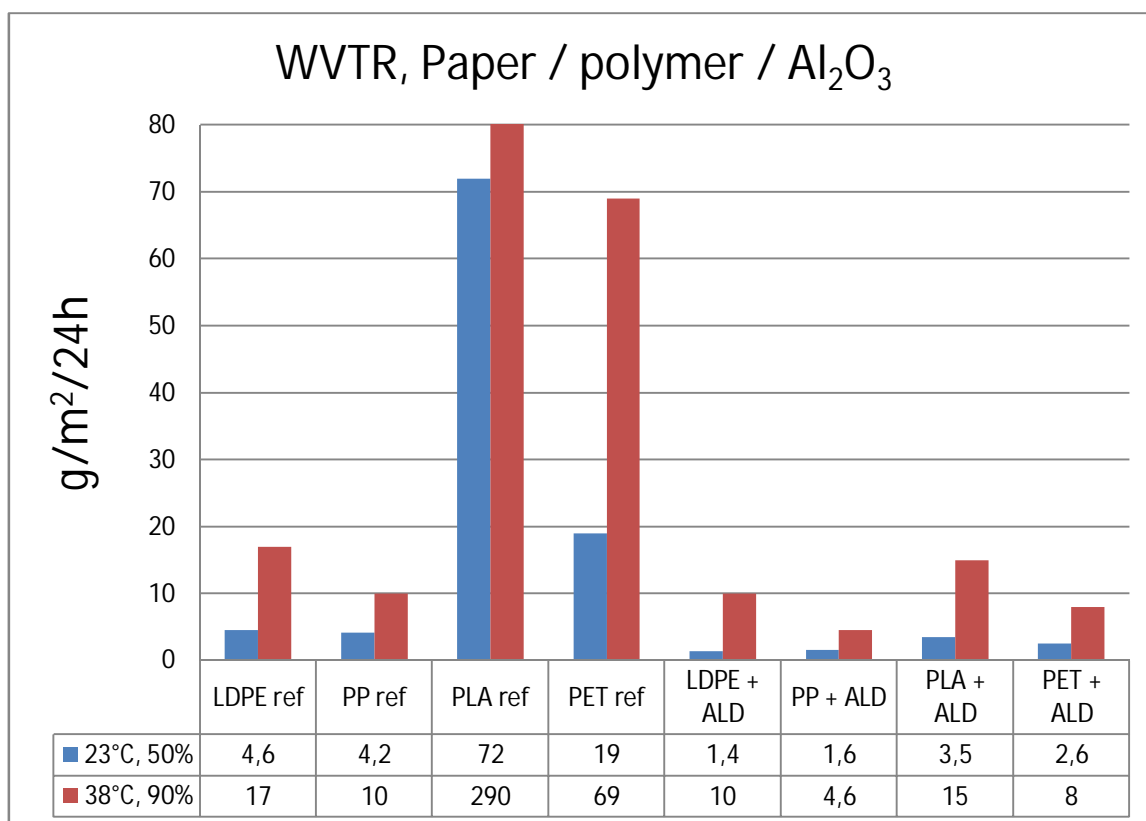


Figure 5.2.1. Comparison of WVTRs of polymers with and without a CALD layer.

Figure 5.2.1 indicates huge difference between the references, and highest values were cut out. The WVTR values with an Al<sub>2</sub>O<sub>3</sub> CALD layer are at much lower level compared to the references. Although the PLA was the poorest reference, there was a significant improvement in the WVTR also in this case.

The relative improvement in the WVTR is again compared in the table 5.2.1. The measured WVTR values of the polymers were divided by the values obtained with a CALD layer in normal and tropical conditions.

Table 5.2.1. Relative improvement in the WVTR with an Al<sub>2</sub>O<sub>3</sub> ALD layer.

	LDPE	PP	PLA	PET
23°C, 50 % RH	3,3	2,6	21	7,3
38°C, 90 % RH	1,7	2,2	19	8,6

Al<sub>2</sub>O<sub>3</sub> CALD layer on PLA provided the biggest improvement (19 and 21 times) in the WVTR. The WVTRs of LDPE and PP were improved with Al<sub>2</sub>O<sub>3</sub> CALD layer only to 1,7 - 3,3 and with PET to 7,3 - 8,6 times lower values. There were no remarkable differences between normal and tropical atmospheric conditions with all the studied polymers.



Figure 5.2.2 shows the results from the oxygen permeability measurements. The reference values are the same as in figure 5.1.9. Relative humidity was 0 % and temperature 23°C. The samples in figure 5.2.2 are similar to the samples in figure 5.2.1.

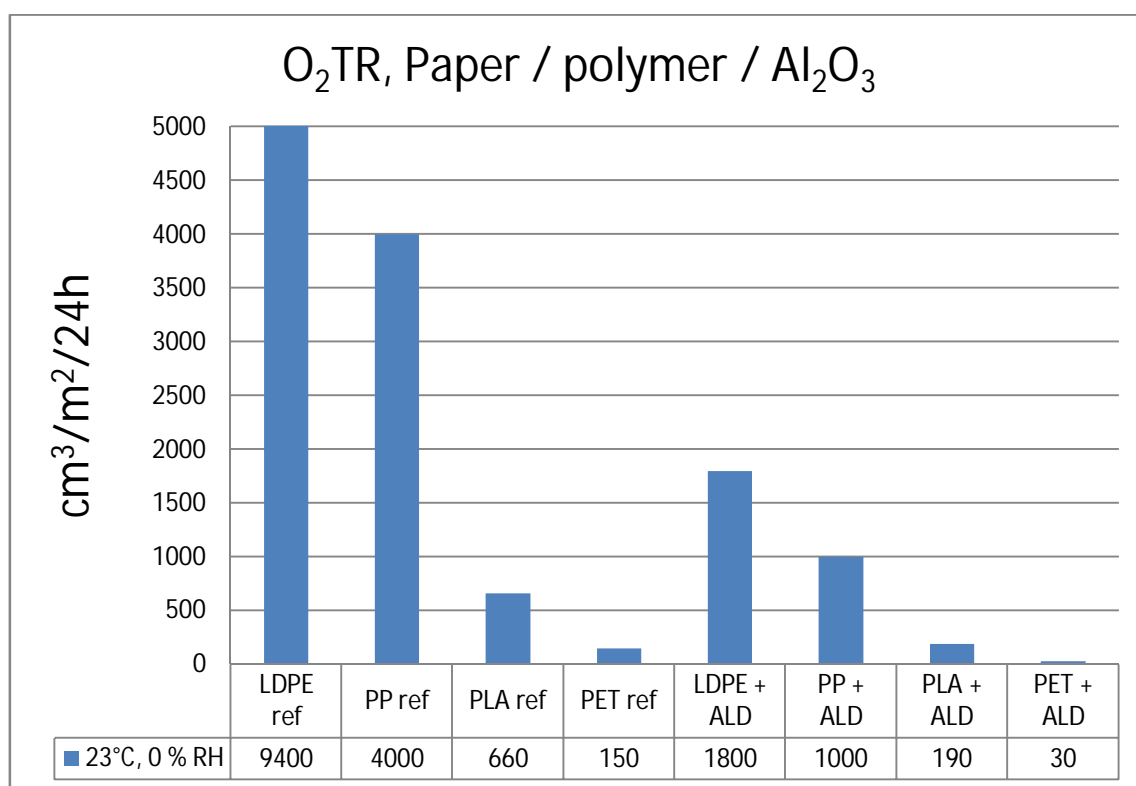


Figure 5.2.2. Comparison of OTRs of polymers with and without a CALD layer.

There were significant differences between the oxygen permeability values of different polymers. Therefore, the maximum value on y axis was set to 5000  $cm^3/m^2/24h$ . PET had clearly the best oxygen barrier with both with and without CALD layer. Table 5.2.2 shows the relative improvements in the OTR with CALD layer in dry conditions.

Table 5.2.2. Relative improvements in the OTR with an  $Al_2O_3$  ALD layer.

	LDPE	PP	PLA	PET
23°C, 0 % RH	5,2	4,0	3,5	5,0

All CALD coated structures have 3,5 - 5,2 time lower value compared to the reference. The relative improvements are close to each other, although, the absolute OTR values show huge differences between the polymers and the polymers with a CALD layer. When the OTR results (figure 5.2.2) are compared to WVTR results (5.2.1.), there is one clear difference. The OTR results with a CALD layer are not at the same level. Instead, they follow systematically the reference values of the tested polymers. More about these studies can be found in an article published by Lahtinen et.al. [40]

### 5.3 Comparison of results from BALD and CALD

This final chapter of permeability results compares the previously presented results. Furthermore, results from the surface energy (5.4) and adhesion (5.5) measurements are shown. The adhesion (peel strength) was measured between the substrate (PET or Al<sub>2</sub>O<sub>3</sub> ALD) and the extrusion coated polymer (PET, PLA or PE). An additional polymer coating on top of the ALD layer can be necessary to protect ALD layer cracking in further converting operations [41]. Other application could require a LDPE sealing layer on top of the Al<sub>2</sub>O<sub>3</sub> ALD layer.

Comparison of permeation values is only shown where BALD and CALD are compared to their references. The equipment, materials and parameters of extrusion coating, ALD process and laboratory analytics were:

Extrusion coating: TUT pilot line, glossy chill roll

Base material: Paper, Lumiflex 90 g/m<sup>2</sup>

Polymers **barrier tests**: **PET** S98 coating weight of 27 g/m<sup>2</sup>, **PLA** coating weight of 25 g/m<sup>2</sup>, **PE** CA7230 and **PP** WF420HMS both coating weight of 30 g/m<sup>2</sup>

Polymers in **adhesion tests**: substrate **PET** S98 coating weight of 30 g/m<sup>2</sup>.

As a coating polymer: **PET** S98 coating weight of 42 g/m<sup>2</sup>, **PLA** coating weight of 28 and 38 g/m<sup>2</sup>, **PE** CA7230 coating weight of 19 and 27 g/m<sup>2</sup>.

**In barrier tests** Batch ALD process: TFS 500, **65°C**

Precursors and layer: TMA and **ozone**, Al<sub>2</sub>O<sub>3</sub>

ALD layer: **1200 cycles**

**In barrier tests** Continuous ALD process: TFS 200R, **100°C**

Precursors and layer: TMA and **water**, Al<sub>2</sub>O<sub>3</sub>

ALD layer: **1000 cycles**

**In adhesion tests** Batch ALD process: TFS 500, **65°C**

Precursors and layer: TMA and ozone, Al<sub>2</sub>O<sub>3</sub>

Measured thickness of ALD layer: **30 - 50 nm**, measured with a spectroscopic ellipsometer (J.A.Woollam M2000FI)

Final Structure in barrier tests: Lumiflex / PET or PLA or PE or PP / Al<sub>2</sub>O<sub>3</sub>

Final Structure in adhesion tests: Lumiflex / PET / (Al<sub>2</sub>O<sub>3</sub> /) PET or PLA or PE

**WVTR: Aquatran 23°C, 50 % RH and 38°C, 90 % RH**  
50 cm<sup>2</sup>, 2 parallel samples

**OTR: OxTran, 23°C and 0 % RH**  
5 cm<sup>2</sup>, 2 parallel samples

**Adhesion test in Hounsfield:** 4 or 5 parallel samples with size of 14 x 130 mm.  
Peeling: angle 90°, speed 40 mm/min, distance 20 mm and maximum force of 10 N.

The results of the moisture barrier measurements are presented in figures 5.3.1 and 5.3.2.

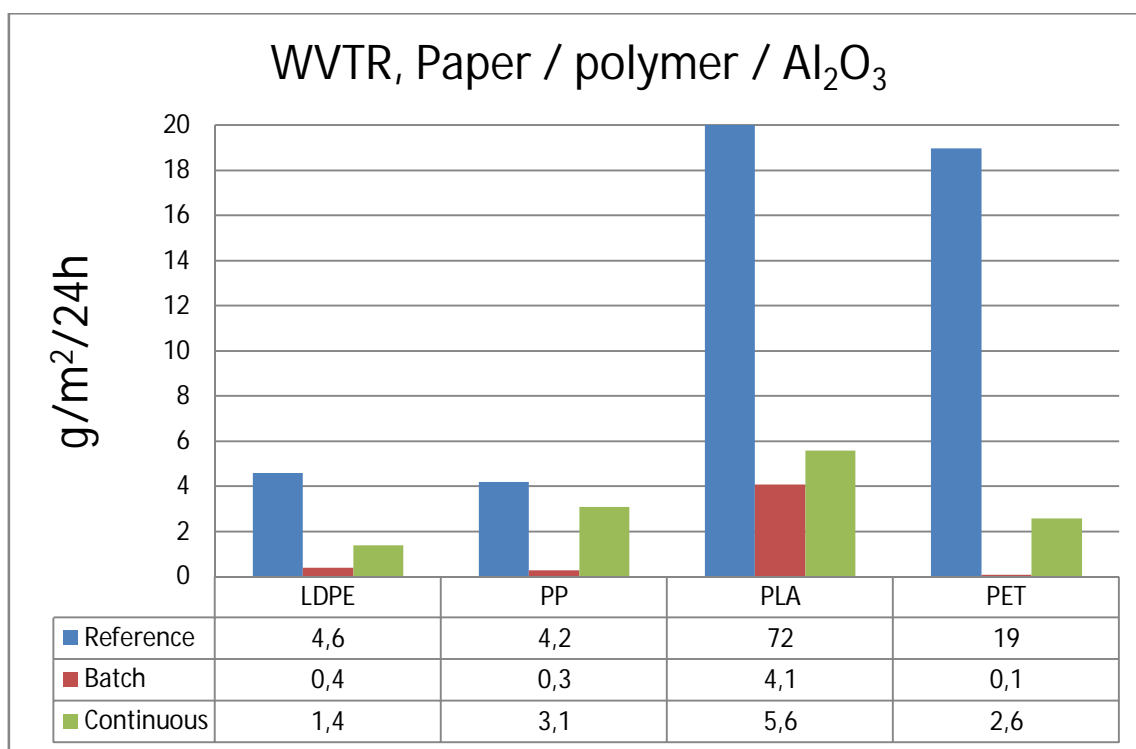


Figure 5.3.1. Comparison of water vapor permeability values for polymers with a BALD or CALD layer and without an ALD layer in normal conditions.

There was a considerable difference between the water vapor permeation values from the BALD and CALD processes (figure 5.3.1). Batch process always produced a better moisture barrier in normal conditions. The reference value of PLA was much higher compared to the others, which could partly explain the poorer moisture barrier with ALD coated PLA.

However, the improvement in PLA's WVTR in CALD was much higher compared to other polymers. PET seemed to be a very good substrate for ALD because its WVTR reaches about the same level as LDPE and PP with an ALD layer. PET with a BALD layer had an extremely good relative improvement in water vapor permeability at 23°C and 50 % RH (table 5.3.1).

Table 5.3.1. Relative improvements in WVTR with an Al<sub>2</sub>O<sub>3</sub> ALD in 23°C, 50 % RH.

$$\frac{\text{WVTR (polymer)}}{\text{WVTR (polymer + Al}_2\text{O}_3 \text{ ALD)}}$$

	LDPE	PP	PLA	PET
BALD	12	14	18	190
CALD	3,3	1,4	13	7,3

Batch process produced systematically better WVTRs in normal conditions. Figure 5.3.2 presents a comparison between the water vapor permeation values in tropical conditions after the BALD and CALD processes.

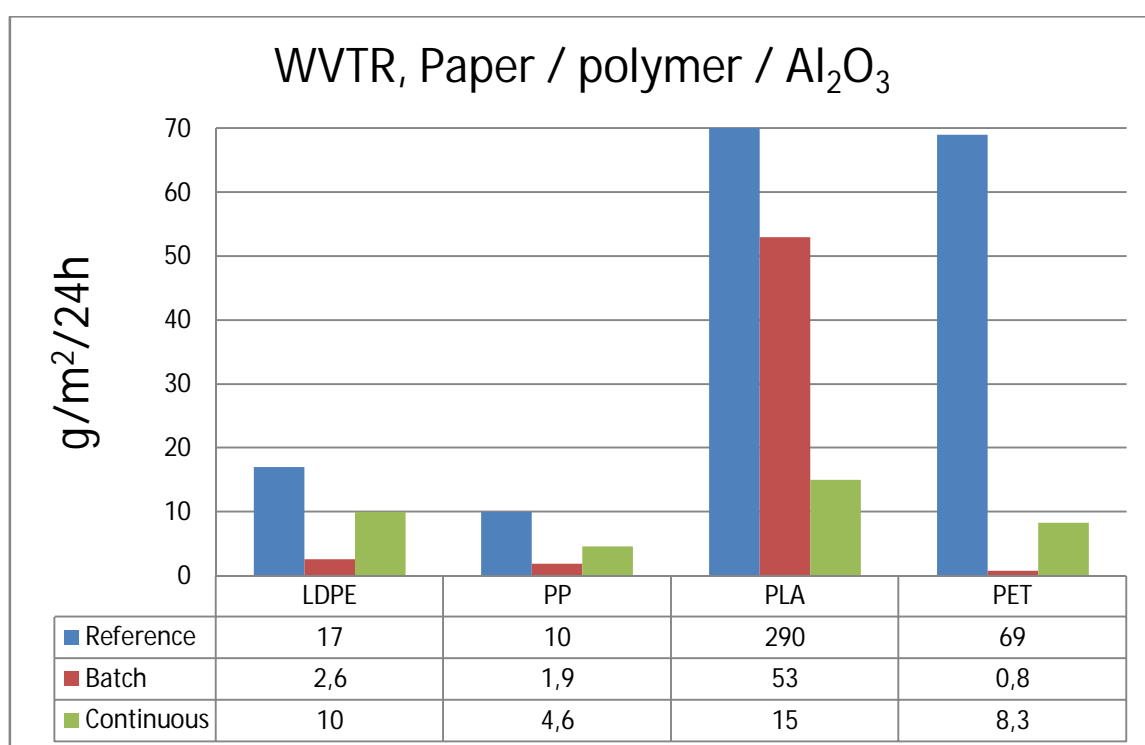


Figure 5.3.2. Comparison of water vapor permeability values for polymers with a BALD or CALD layer and without an ALD layer in tropical conditions.

Figure 5.3.2 shows the WVTR values in tropical conditions after the batch and continuous ALD process. Batch process produced again lower WVTR values with the exception of PLA. It seems that a moisture barrier with the batch process ALD on PLA was very poor when compared to the other polymers. It can be noticed in figure 5.1.5 that the BALD process with 1200 cycles led to a moisture permeability of 53 g/m<sup>2</sup>/24h while with only 600 cycles the value was 55 g/m<sup>2</sup>/24h. It is thus possible that there were defects in these PLA samples after 1200 cycles in the BALD.

PET with a BALD layer shows an excellent improvement in WVTR in tropical conditions. Table 5.3.2 presents the relative improvements in the WVTR in tropical conditions.

Table 5.3.2. Relative improvements in the WVTR with an Al<sub>2</sub>O<sub>3</sub> ALD layer in 38°C, 90 % RH.

$$\frac{\text{WVTR (polymer)}}{\text{WVTR (polymer + Al}_2\text{O}_3 \text{ ALD)}}$$

	LDPE	PP	PLA	PET
BALD	6,5	5,3	5,5	86
CALD	1,7	2,2	19	8,3

There were differences in the process parameters between the batch and continuous ALD. Besides different kinds of ALD devices, the number of deposition cycles, processing temperatures and oxidizing precursor gases with TMA were also different. Thus, there were many possible causes for different results. It is impossible to state which parameter had the greatest influence on the measured permeability values.

A possible reason for the better barrier values in the BALD process compared to the CALD was the ALD process temperature. Appendices 1 and 2 show the IR-spectra from PLA films stored in two different temperatures (65 or 100°C) and 9 different amount of time in minutes (0, 0.5, 1, 5, 20, 30, 60, 120 and 300) in the oven. Figure 5.3.3 shows some of these PLA samples.



Figure 5.3.3. PLA films kept in an oven at 100°C for a period of time written above the samples.

There was a clear difference in spectra (between 910 and 930  $\text{cm}^{-1}$ ) between the samples kept at 65°C and 100°C (Appendix 1 and 2). Five minutes at 100°C was enough to change the crystallinity of the film. The film was in the CALD process chamber (TFS 200R) for a longer time than 5 minutes before the deposition process was started. Thus, the film was partly crystallized before ALD coating. A partly crystalline PLA surface might have been better substrate to an  $\text{Al}_2\text{O}_3$  ALD coating than a completely amorphous PLA. The temperature in both the BALD and CALD processes should have been the same if the target is to compare the achieved permeability values to each other.

The same comparison was also made regarding the oxygen transmission rate. Figure 5.3.4 shows the compiled results of the oxygen permeability measurements.

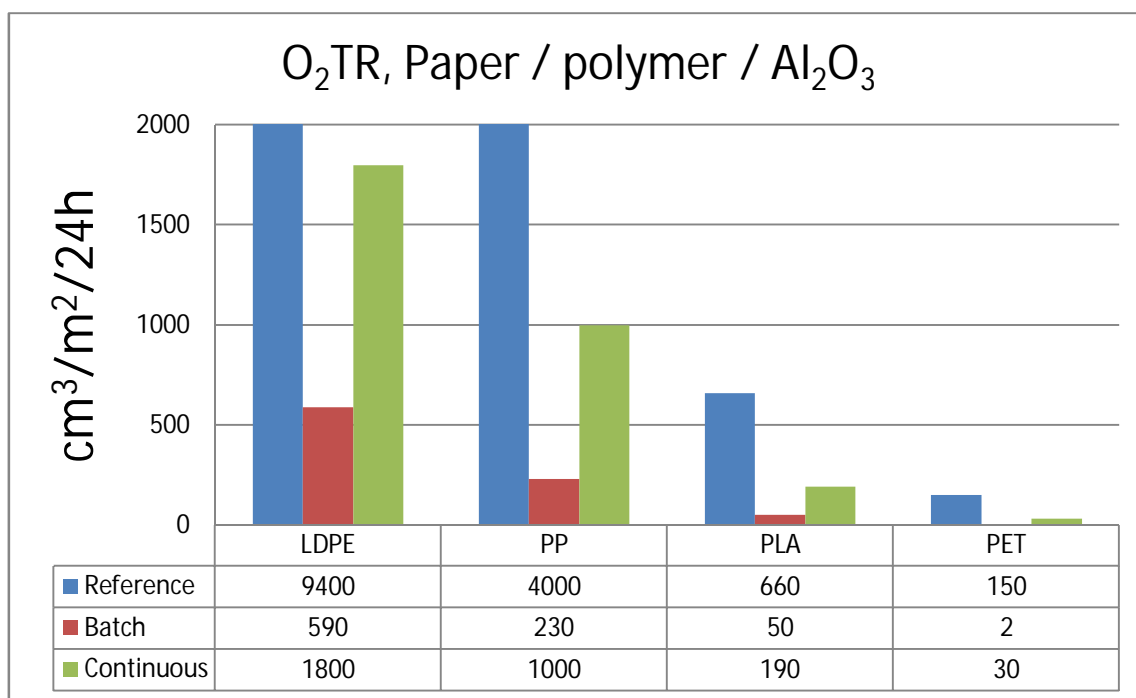


Figure 5.3.4. Compiled OTR values for the coated polymers with a BALD or CALD layer and without an ALD layer.

The OTR results were constantly at a lower level when the  $Al_2O_3$  layer was deposited by the batch method. The batch process with more cycles, a lower temperature and with an ozone precursor produced a better oxygen barrier compared to the continuous process with water as the oxidizing precursor. However, it was impossible to estimate the effect of each parameter on the oxygen barrier.

Table 5.3.3 presents the relative improvements in the OTRs.

Table 5.3.3. Relative improvements in the OTR with an  $Al_2O_3$  ALD layer in 23°C, 0 % RH.

$$\frac{OTR(\text{polymer})}{OTR(\text{polymer} + Al_2O_3 \text{ ALD})}$$

	LDPE	PP	PLA	PET
BALD	16	17	13	75
CALD	5,2	4,0	3,5	5

PET shows an excellent improvement in the OTR after BALD coating. One target in the future studies should be to find the optimal values for the key ALD process parameters when targeting for as good barrier properties as possible for polymer film. WVTR and OTR must be dealt with separately, because they are behaving differently.

A comparison of WVTR and OTR results in this study to the results of Hirvikorpi et al. (table 3.3) with fiber / PLA / Al<sub>2</sub>O<sub>3</sub> ALD layer is shown here after. Hirvikorpi used temperatures of 80°C and 100°C, while 65°C and 100°C were used here as the ALD process temperatures with ozone and water as the second precursor, respectively. The first precursor in all the ALD processes was always TMA. The results are compared in table 5.3.4.

Table 5.3.4. Measured permeability of fiber + PLA + Al<sub>2</sub>O<sub>3</sub> ALD in 23°C: WVTR (with 35 g/m<sup>2</sup> in 75 % RH and with 25 g/m<sup>2</sup> in 50 % RH) and OTR (with 35 g/m<sup>2</sup> in 50 % RH and with 25 g/m<sup>2</sup> in 0 % RH)

WVTR [g/m <sup>2</sup> /24h]	OTR [cm <sup>3</sup> /m <sup>2</sup> /24h]	
1 ± 0,2	20 ± 3	First four are from the study of Hirvikorpi
5 ± 2	12 ± 1	PLA 35 g/m <sup>2</sup> in 100 °C with water precursor [9]
3 ± 1	6 ± 1	PLA 35 g/m <sup>2</sup> in 100 °C with ozone precursor [9]
7 ± 2	3 ± 1	PLA 35 g/m <sup>2</sup> in 80 °C with water precursor [9]
6 ± 2	200 ± 100	PLA 35 g/m <sup>2</sup> in 80 °C with ozone precursor [9]
4 ± 1	50 ± 10	PLA 25 g/m <sup>2</sup> in 100 °C with water precursor
		PLA 25 g/m <sup>2</sup> in 65 °C with ozone precursor

The fifth line in table 5.3.4 is the only which was from the CALD trials instead of the BALD. The influence of precursor to the WVTR of the structure was not the same in these two studies. Hirvikorpi achieved lower WVTR values with water as the oxidizing precursor, but in this study the ozone as the second precursor brought a slightly lower WVTR values to the structure. This could be due to different ALD devices and process parameters, difference between the CALD and BALD processes or different substrates. The reason didn't seem to be deposition temperature. Hirvikorpi measured higher WVTR values for the same PLA film thickness, when the ALD process temperature was decreased from 100°C to 80°C.

The influence of the oxidizing precursor and the deposition temperature to the OTR was similar in these two studies, but the difference in the OTR values was remarkable. An ozone precursor and a lower ALD process temperature led to lower oxygen permeability. The difference in the ALD processes and the substrates was so significant when comparing the WVTR and OTR values that it cannot be said for sure which parameter had the most significant effect on the permeability values.



## 5.4 Surface energies of Al<sub>2</sub>O<sub>3</sub> ALD substrates

Surface energies of ALD coated substrates (figure 5.4) were calculated from the contact angles (CA) with the test liquids [41]. Six parallel CA measurements were performed with each test liquid to obtain reliable results. The equipment used in the test was KSV CAM 200. The number (0, 75 or 150) after PET or ALD surface indicates how effective (Wmin/m<sup>2</sup>) corona pre-treatment was used for that specific sample.

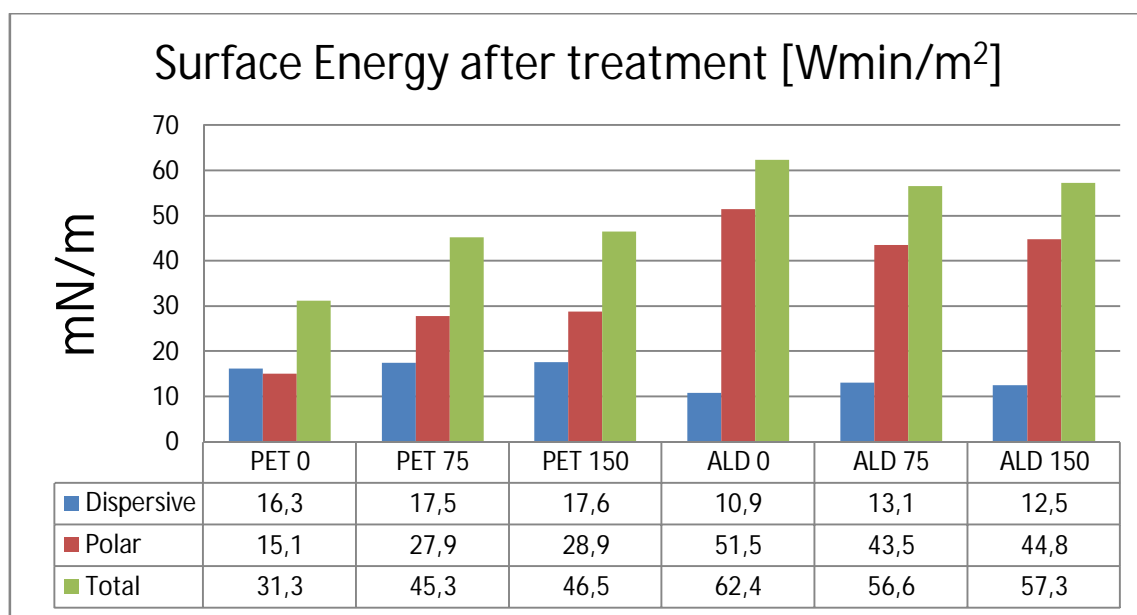


Figure 5.4. Comparison of surface energies after corona pre-treatment on the surface.

Figure 5.4 indicates clear difference when comparing uncoated and ALD coated PET surface. PET had a high dispersive energy component, but the polar component was much smaller than Al<sub>2</sub>O<sub>3</sub>, and the total surface energy of PET (31,3 mN/m) was about half of that with Al<sub>2</sub>O<sub>3</sub> (62,4 mN/m).

Corona treatment increased the polar energy component of PET surface, which led to an increased total surface energy. Corona treatment decreased the polar energy component of Al<sub>2</sub>O<sub>3</sub> somewhat which decreased the total surface energy slightly, although the dispersive component increased a bit. The biggest difference between surfaces was that corona treatment increased the surface energy of PET and decreased the surface energy of Al<sub>2</sub>O<sub>3</sub> ALD coated PET.

There were relatively small differences in the surface energies of uncoated and coated PET after the corona pre-treatments. However, a lower pre-treatment efficiency level would be more feasible, because too high corona efficiency may lead to a jumping spark through the paper / PET structure. This can create pinholes to the PET film. Pinholes in the polymer film are a huge problem in the ALD, when the target is to achieve as good barrier properties as possible.

## 5.5 Adhesion of extrusion coating to Al<sub>2</sub>O<sub>3</sub> ALD substrate

The surface energy measurements were followed by the adhesion studies. The same substrate materials were used as in the surface energy measurements, and the influence of corona pre-treatment before extrusion coating was studied at the efficiency of 75 Wmin/m<sup>2</sup>. Uncoated and Al<sub>2</sub>O<sub>3</sub> coated PET were extrusion coated with two coat weights of LDPE, PLA and PET. Table 5.5 presents the structures with coat weight, the corona power and adhesion [42]. Measurements were made with Hounsfield, and there were four or five parallel measurements for each sample.

Table 5.5. Adhesion (peel strength) of extrusion coated polymers to PET and Al<sub>2</sub>O<sub>3</sub> ALD surface (deviations in parentheses).

	Adhesion (N/m) corona OFF	Adhesion (N/m) corona ON
PET / PE 19 g/m <sup>2</sup>	47 (2.7)	perfect
PET / PE 27 g/m <sup>2</sup>	69 (2.2)	perfect
PET / PLA 28 g/m <sup>2</sup>	13 (1.8)	20 (2.6)
PET / PLA 38 g/m <sup>2</sup>	9.8 (1.1)	19 (2.9)
PET / PET 42 g/m <sup>2</sup>	perfect	perfect
Al <sub>2</sub> O <sub>3</sub> / PE 19 g/m <sup>2</sup>	34 (2.9)	perfect
Al <sub>2</sub> O <sub>3</sub> / PE 27 g/m <sup>2</sup>	130 (47)	perfect
Al <sub>2</sub> O <sub>3</sub> / PLA 28 g/m <sup>2</sup>	5.1 (0.4)	26 (0.8)
Al <sub>2</sub> O <sub>3</sub> / PLA 38 g/m <sup>2</sup>	6.8 (2.2)	25 (2.9)
Al <sub>2</sub> O <sub>3</sub> / PET 42 g/m <sup>2</sup>	0	8.1 (1.9)

Table 5.5 shows that LDPE was an optimal polymer on top of the Al<sub>2</sub>O<sub>3</sub> ALD surface, because adhesion was perfect when corona treatment was used. PLA and PET are not as good as LDPE as a sealing layer in packages because of their higher melting temperatures.

PLA and PET had poor adhesion to the Al<sub>2</sub>O<sub>3</sub> ALD substrate. Corona pre-treatment improved the situation only slightly. Al<sub>2</sub>O<sub>3</sub> ALD had a significant impact on adhesion because extrusion coated PET had a perfect adhesion to PET substrate without the Al<sub>2</sub>O<sub>3</sub> ALD layer. Presumably the reason for the perfect adhesion between the extrusion coated LDPE and the Al<sub>2</sub>O<sub>3</sub> ALD layer was the oxidation of LDPE in the air gap. Therefore LDPE created strong bonding with a corona pre-treated aluminum oxide surface.

These results encourage continuing studies with a LDPE layer as a sealing layer on top of the Al<sub>2</sub>O<sub>3</sub> ALD layer. Same kind of studies has been presented at TAPPI PLACE 2012 by K. Lahtinen [43]. However, LDPE was used as a substrate instead of PET. Like in this thesis, Lahtinen had an Al<sub>2</sub>O<sub>3</sub> ALD layer and LDPE was extrusion coated on top of the ALD layer.

## 6 CONCLUSIONS

The most significant benefit for the ALD layer in packages in the future might be cost savings. Dramatic reduction in the weight of the package provides savings for the companies. Even if the ALD process would be slightly more expensive than the old laminating process, the cost savings will come from lower transportation costs and the material savings. Transportation is cheaper because the recyclable [44] empty package is lighter to carry to the collecting place than taking a heavier package to the dump site. Material savings is gained also with thinner polymer layer because the required barrier properties are achieved with the ALD layer.

This thesis indicates that an  $\text{Al}_2\text{O}_3$  ALD layer improves the water vapor and oxygen barrier properties of LDPE, PP, PLA and PET films significantly. Especially PET is an excellent substrate for the ALD, when the target is to achieve as good barrier as possible. An  $\text{Al}_2\text{O}_3$  ALD layer on top a PET film can decrease both the WVTR and the OTR to 100 times lower values than the pure PET film shows. The film with the  $\text{Al}_2\text{O}_3$  ALD layer can be further extrusion coated with an extra layer of LDPE layer to create a structure having good sealing properties. The  $\text{Al}_2\text{O}_3$  ALD layer doesn't have to be thicker than 40 – 50 nm to improve the WVTR of LDPE, PP or PET film to a value well below  $1 \text{ g/m}^2/24\text{h}$  in normal conditions. More studies should be carried out especially with PLA under the  $\text{Al}_2\text{O}_3$  ALD layer. The barrier values were encouraging, when the CALD process temperature was  $100^\circ\text{C}$ . With such a structure it is also possible to prepare completely biodegradable material.

Producing an ALD layer using the batch or the continuous process is so expensive that it is not cost-effective for packages today. The ALD process technology is not ready for the Roll-to-Roll solutions yet, but research scientists both in universities and companies are working hard with this challenge. There are good examples (e.g. WCS 500) of the research and development work with the target to build a profitable RRALD device to the markets potentially decreasing the cost per package in the future. It is obvious that the mass production with ALD process will take place in the future. The fierce competition between the machinery suppliers will create many kinds of solutions because packaging is a huge business globally. There is also an opportunity to increase employment in the packaging research both in Finland and in Europe. Maybe development will generate a new big employer, which will also concentrate to protect the nature around the world with biopolymer products.

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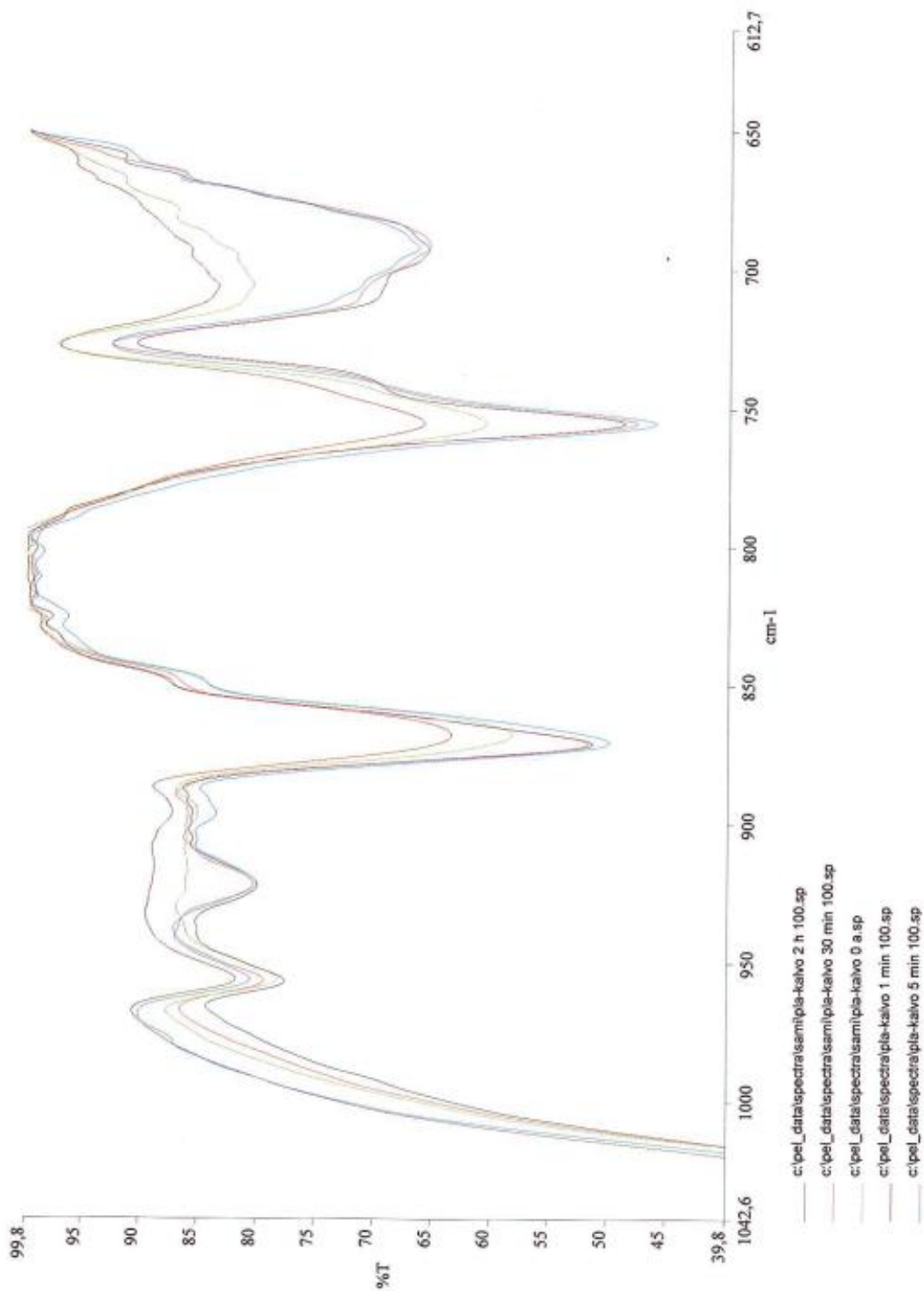
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## APPENDIX 1

PLA's IR-spectroscopy in 100°C.





## APPENDIX 2

PLA's IR-spectroscopy in 65°C and in 100°C.

