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ATOMIC LAYER DEPOSITED THIN BARRIER FILMS FOR PACKAGING

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Atomic layer deposition (ALD) is a surface controlled layer-by-layer process based on self-limiting gas-solid reactions. Thin films are prepared using volatile precursors in repeating cycles until a preferred thickness is obtained. ALD suites for producing dense and pinhole-free inorganic films uniform in thickness. The most important commercial application area today is in microelectronics. The purpose of this paper is to demonstrate the potential and the challenges of using ALD for packaging materials. ALD can have a profound effect on the barrier properties and it can also be used to create antimicrobial thin films. Due to the brittle nature of inorganic thin films, these have to be protected with a polymer layer, also providing heat sealing properties. Although ALD is today carried out primarily in batch mode, the ongoing development of roll-to-roll processes will enhance the techno-economic feasibility of ALD, among others, for packaging materials.

Keywords: atomic layer deposition, barrier, migration, packaging, polymer, safety, thin film

INTRODUCTION

The atomic layer deposition (ALD) technique is based on repeated cycles of self-limiting reactions between precursor gases and a solid surface.[1-3] The precursors are pulsed into the reactor chamber alternately, separated by inert gas pulses to remove other than chemisorbed precursors. During one deposition cycle, only one monolayer is deposited on an ideal surface. These cycles are then repeated until a specific layer thickness is obtained. ALD is suitable for producing conformal, dense and pinhole-free inorganic thin layers. The most important current application area for ALD is microelectronics. Future applications include, for example, printed flexible electronics, membranes for environmental applications, catalysts, solar cells and other energy applications.

The purpose of this paper is to demonstrate both the potential and the challenges of using ALD for packaging materials. If this technique could be used to replace aluminium foil or decrease the thickness of the polymer layers in packaging laminates, this would lead to improved material/energy recovery and lighter packaging materials. There is also a demand for renewable packaging materials. However, the barrier properties of these materials, especially against moisture, are not yet on a sufficient level for more demanding packaging applications. ALD films have shown to provide various materials with enhanced diffusion barrier against, for example, vapours and gases and also antibacterial activity.[4-13] ALD can also be used as a surface treatment method to adjust hydrophobicity and to improve printability of plastic surfaces.[14-16] A thin Al_2O_3 layer does not impair disintegration of PLA film or coated board, and polymer granules deposited with thin oxide layers have been melt processed into composites, indicating a certain level of recyclability.[17,18]

ALD utilizes today primarily batch reactors with vacuum chambers for coating of stationary objects. However, roll-to-roll reactors and atmospheric processes are being developed by different research groups and equipment suppliers.[19-27] A techno-economically feasible roll-to-roll process is a necessity for utilizing ALD for packaging material webs, such as plastic films, coated papers and boards, and laminates. In one roll-to-roll process, two precursor chambers (A and B) are separated by a purge chamber (P). The material web to be coated travels back and forth through these chambers in an A-P-B-P-A-P-B- mode. Alternatively, a die with multiple channels can be used for feeding precursor and purging gases. Then either the die and/or the

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material web moves in relation to each other. Atmospheric reactors are based on replacing air from the reaction zone with inert gas.

Concerns on food safety and quality, and the need for extended shelf-life of packaged foods have promoted the development of novel packaging materials. When developing new materials for food contact,product safety and compliance of the materials with the current legislative requirements should be taken into account already during the product development phase. The current legislation reflects the existing packaging solutions and materials and thus it is not totally feasible for new materials and technologies. In such cases, authorization may be needed before a new raw material can be used for producing new packaging solutions.

All food contact materials (FCM) are regulated with the Framework Regulation[28] and with the GMP Regulation.[29] For plastic food contact materials, the Plastics Regulation[30] should be followed. The regulation applies to materials and articles consisting purely of plastics, as well as combinations of plastics and other materials. Both types may also be covered by a coating, as is the case with ALD coated plastic 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.[30] However, if there is any potential health risk, their use should be assessed by the manufacturer of the FCM. The migration of a substance not listed among authorized substances should not exceed the limit of 0.01 mg/kg food. Today a declaration of compliance is not required for coatings, however, adequate information should be provided to the manufacturer of the packaging material or package to ensure compliance for substances to which restrictions, e.g. specific migration limits, are given. In addition, substances known to be mutagenic, carcinogenic or toxic to reproduction must not be used in FCMs, and today substances in nanoform are allowed only when authorized. In EU, a nanomaterial is defined for regulatory purposes 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" by the European Commission.[31] At the moment, this definition is subject to re-evaluation.[32,33]

This paper is mainly based on the final report of project "Roll-to-roll atomic layer deposition development" by Vähä-Nissi *et al*.[34] with further details, and references to several publications and conference presentations.

EXPERIMENTAL

Thin film deposition

Atomic layer deposition of inorganic and hybrid thin films was carried out in a commercial Picosun SUNALE^{TM} batch reactor in a semi-clean test environment. Deposition temperature was 50-100 ºC. The precursors for Al_2O_3 were water, ozone and trimethylaluminium (TMA - $Al(CH_3)_3$, SAFC Hitech, electronic grade purity), while ethylene glycol (min. purity of 99.5%, Riedel de-Haën) and DL-lactic acid (Sigma Aldrich) were used as organic precursors in the hybrid layers. Details about the hybrids have been presented earlier.[12,16] High purity nitrogen was used as a carrier and purge gas.

The plastic films used are described in Table 1 and coated board samples in Table 2. BOPP, O-PET and PLA films were three-layer structures: a core layer sandwiched between two thin skin layers. Cellophane is antistatic and dimensionally stable. PLA has a glass transition temperature of 60-65 °C, while for cellophane this is higher and undefined. Please contact the suppliers for further information about these plastic films.

Table 1
Description of film samples used in the study

Film	Description	Source
A-CEL	Anchored uncoated 15 µm cellophane film	Innovia Films Ltd
CEL	NatureFlex^{TM} 42 NP (transparent 42 µm cellophane film)	Innovia Films Ltd
C-CEL	NatureFlex^{TM} 45 NVL (both side coated 45 µm cellophane film)	Innovia Films Ltd
BOPP	Rayoface^{TM} 50C (biaxially oriented 50 µm polypropylene film)	Innovia Films Ltd
PHB/HV	BV301050 (50 µm polyhydroxybutyrate/hydroxyvalerate film)	Goodfellow Ltd
O-PA	Opalen 65 (15 µm oriented polyamide + 50 µm polyethylene)	Bemis Company
O-PET	OPET 23 (biaxially oriented 12 µm polyethylene terephthalate film)	Bemis Company
PLA	Evlon® EV 40 (biaxially oriented 40 µm polylactic acid film)	BI-AX International
PE	Borstar FB2310 linear low density polyethylene film	Borealis Polymers

Table 2
Description of board samples used in the study

Board	Base board	Coating	Coated
B/PLA	210 g/m^2 Cupforma Classic	30 g/m^2 polylactic acid (PLA, experimental grade)	Extrusion coating pilot line at Tampere Univ. of Tech.
B/PE	210 g/m^2 Cupforma Classic	30 g/m^2 low density polyethylene (CA7230, Borealis Polymers)	Extrusion coating pilot line at Tampere Univ. of Tech.
B/PEC	250 g/m^2 EnsoCoat	Pectin/nanoclay mixture (5% pectin and 2% of nanoclay)	SutCo pilot line, VTT, Espoo
B/LSW B/LHW	210 g/m^2 Cupforma Classic	10-15 g/m^2 soft (SW) and hard wood (HW) kraft lignin laurate	Laboratory coating, VTT

Sample characterization

Thin film thickness on polymer films could not be directly measured. Thermal sensitivity, surface roughness and optical properties of the polymers prevented the use of currently available analyzing methods. Therefore, apparent thicknesses were determined with single wavelength ellipsometry (SE400adv, Sentech Instruments GmbH, angle of incidence of 70°) for thin films deposited with the same process parameters on silicon wafers. Due to the different surface chemistries, the actual growth rate on the polymers may, however, deviate from that determined on a silicon wafer.[35-37]

Oxygen transmission rates (OTR) were determined with Systech M8001 and Mocon Oxtran 2/20 at 23 °C and either 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 oxygen was then introduced into the outside chamber of the diffusion cell. The flux of oxygen diffusing through the sample to the inside chamber was conveyed to the sensor. OTR was expressed as cm^3/m^2/10^5 Pa/d. At least two parallel measurements were carried out for each sample.

Water vapour transmission rate (WVTR) refers to the amount of water vapour 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% relative humidity. The values were expressed as g/m^2/d. Three parallel measurements were performed for each sample. Values below 1 g/m^2/d were out of range for this test setup.

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.

Mechanical properties were studied, for example, at Aalto University by straining samples in a mechanical tensile tester 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 percent. 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. 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.

Migration of aluminium from ALD layers was studied with typical simulants used in testing of 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 10 days. The volume of simulant per surface area of the sample was 100 ml/dm^2. Simulants without samples were used as references. Al content in the simulant was analyzed using inductively coupled plasma-mass spectrometry (ICP-MS). The 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.

RESULTS AND DISCUSSION

Barrier properties

Several of the samples had a WVTR below the measuring accuracy of the gravimetric method used. However, the best oxygen barriers with a thin Al_2O_3 layer were PHB/HV and O-PET films, and the best water vapor barriers BOPP, O-PA, O-PET and PLA films (Table 3). However, the most significant overall improvements in barrier values were observed with A-CEL, PLA, PHB/HV and O-PET films. This indicated that proper surface chemistry, and specifically oxygen containing groups, 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 also sites for chain scission and formation of other functional groups. The films with the most enhanced barrier properties after the ALD had also high relative polarities of surface energy (Table 4).

Replacing water with ozone as 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 a more uniform but also a more polar oxide layer. In addition, ozone does not leave hydrogen impurities in the deposited Al_2O_3 layer. The growth rate with ozone was similar to lower than that with water. Somewhat better oxygen barrier properties have been also achieved earlier with ozone than with water.[9]

Table 3
OTRs and WVTRs for polymer films with 25 nm of ALD Al_2O_3 deposited at 100 °C

	OTR (23 °C, RH 50%) $cm^3/m^2/10^5$ Pa/d		WVTR (23 °C, RH 50%) $g/m^2/d$	
Oxidizing precursor	Water	Ozone	Water	Ozone
A-CEL	400		290	
+ 25 nm ALD Al_2O_3	4.9	9.5	< 1.0	11
CEL	16		100	
+ 25 nm ALD Al_2O_3	8.9	< 0.1	44	18
C-CEL	12		35	
+ 25 nm ALD Al_2O_3	5.6	< 0.1	2	2.4
BOPP	1300		< 1.0	
+ 25 nm ALD Al_2O_3	4.5	6.2	< 1.0	< 1.0
PHB/HV	> 400		8.3	
+ 25 nm ALD Al_2O_3	2.1	< 0.1	1.0	-
O-PA	53		< 1.0	
+ 25 nm ALD Al_2O_3	10	0.2	< 1.0	< 1.0
O-PET	68		3.1	
+ 25 nm ALD Al_2O_3	2.3	< 0.1	< 1.0	< 1.0
PLA	> 400		21	
+ 25 nm ALD Al_2O_3	4.5	< 0.1	< 1.0	< 1.0

Table 4
Surface energy and relative polarity of tested films

Film	Surface energy, mN/m			Polarity, %
	Dispersive	Polar	Total	
A-CEL	34.6	13.4	48.0	33.5
CEL	33.6	36.3	69.9	52.0
C-CEL	33.7	5.0	38.7	12.9
BOPP	31.5	5.3	36.9	14.4
PHB/HV	33.8	10.1	43.9	23.0
O-PA	35.5	4.9	40.4	12.1
O-PET	39.9	9.8	49.6	19.8
PLA	34.9	11.1	46.0	24.1

Table 5
Effect of 25 nm Al_2O_3 on the barrier properties of pectin/lignin laurate coated board

Board	Coat weight (g/m^2)	OTR (23 °C, RH 50%) cm^3/m^2/10^5 Pa/d		WVTR (23 °C, RH 50%) g/m^2/d	
			+ 25 nm Al_2O_3		+ 25 nm Al_2O_3
B/LSW	11	58000	3000		
B/LSW	15	36000	1700		
B/LHW	10	55000	2200		
B/LHW	15	37000	3200		
B/PEC	9.2	265	2.5	96	< 1.0
B/PEC	15	1	<0.1	67	< 1.0

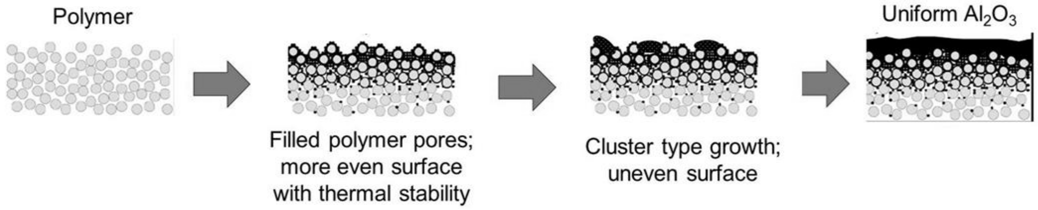

Figure 1: Growth of Al_2O_3 thin layer on polymer surfaces by ALD (modified from Wilson *et al.*[38])

Paperboards coated with lignin laurate dispersions (B/LSW and B/LHW) provided no good oxygen barriers, and although oxygen barrier was significantly improved by 25 nm Al_2O_3, the values were not good enough for several packaging applications (Table 5). This was probably due to the poor uniformity of the lignin coatings. Paperboards coated with pectin/nanoclay mixture (B/PEC) proved to be a potential alternative. The coat 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 Al_2O_3 was due to the enhanced uniformity and smoothness of the PEC coating with increasing coat weight. ALD reactor temperature was 100 ºC and deposition was performed with TMA and water.

Optimization of material and process parameters

Nucleation and growth of thin films on non-ideal polymer surfaces at low temperatures is complicated, as presented in Figure 1. Precursors react with the accessible polar oxo-groups on and in the polymer during the first deposition cycles.[38-41] This is followed by cluster formation.[37,38,42,43] As the number of deposition cycles increases, these clusters merge to form islands and eventually a uniform film is achieved. The polar groups, such as carbonyl and hydroxyl, are partly characteristic of the polymer itself and partly created by surface pretreatments, additives and polymer degradation during processing. In addition, water and reaction by-products can create additional reaction sites. Comparison between the PLA and BOPP films showed that in spite of a smoother surface, more aluminium was deposited on the more polar PLA.[37] The decrease in the relative number of carbon-oxygen groups and change in the softening temperature also indicated chemical interactions between PLA and TMA. The following examples show how to make use of material and process parameters to affect thin film growth and properties.

Corona and argon plasma pretreatments prior to the ALD had a positive effect on the Al_2O_3 layers on B/PE and B/PLA (Figure 2), which was also supported by our previous study.[10] Thinner films are more sensitive for the early film growth and 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 and plasma are commonly used in various industrial applications, such as paper and film converting to adjust surface polarity and wetting characteristics. Corona treatment has several beneficial effects, the most significant of which is the formation of oxidized groups.[44] 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. The treatment level at the SutCo pilot line was 50 Wmin/m^2. ALD deposition was performed with TMA and water at 80 °C immediately after the pretreatment. It is important that the treated plastic film have neither time nor possibility to attract particulate contaminants before thin layer deposition.

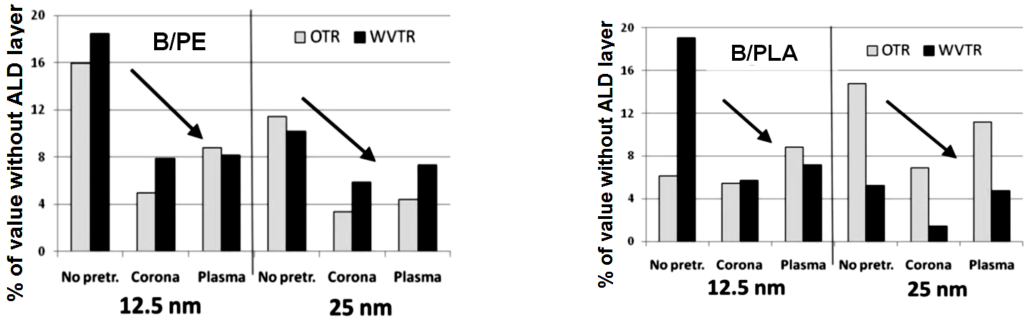

Figure 2: Relative improvements in water vapor and oxygen barriers by corona and argon plasma pretreatment of B/PE (left)[17] and B/PLA (right) prior to ALD Al_2O_3 with TMA and water at 80 ºC

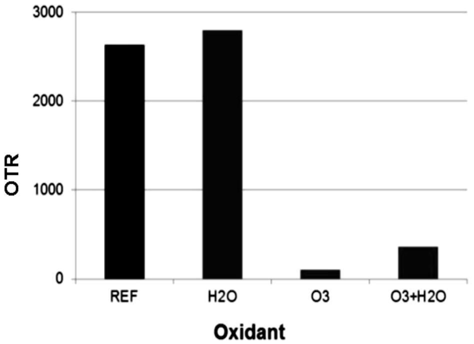

Figure 3: Oxygen barrier of PE film with an antioxidant additive (REF) after Al_2O_3 deposition with TMA-water (H_2O), TMA-ozone (O_3) and 20 pulses of ozone followed by TMA-water processes (O_3+H_2O)

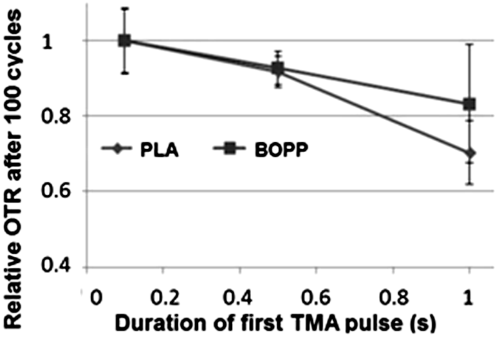

Figure 4: Effect of first TMA pulse length (s) on relative OTR of BOPP and PLA films after further 99 deposition cycles with 0.1 s long TMA pulses

Film additives can be detrimental to ALD. For example, a linear low density polyethylene film with an antioxidant agent (PE film) prevented the growth of Al_2O_3 with the TMA-water process (Figure 3) at 100 °C. However, after 20 pulses of ozone to the reactor, Al_2O_3 layers were grown successfully also with the water process. The TMA-ozone process did not need such a pretreatment. A similar effect has also been observed with an untreated biaxially oriented polypropylene film. However, the results for the corona-treated BOPP and polyethylene film without antioxidant indicated that Al_2O_3 can also be deposited onto polyolefin films with ALD.

Another option is to promote absorption of the precursor 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 (Figure 4). We assumed that such an enhanced absorption of precursor into the polymer and formation of an interphase could lead to a somewhat improved water vapor barrier. However, absorption also improved the oxygen barrier by 20-30%, especially with the more polar PLA film.

The ALD depositions have been performed under different process conditions. The parameters have 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. Typical reactor temperatures tested were between 50-100 °C. Thin films deposited at low temperatures contain typically more impurities than films deposited at high temperatures. These impurities together with lower film density may impair barrier properties. In addition, the overall cycle time is usually longer at low deposition temperatures. Reactor temperature should be as high as possible and yet lower than the temperature at which the polymer degrades, melts or softens. 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, however, 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.

Mechanical properties of ALD layers

Packaging materials are exposed to various mechanical stresses during converting and packaging processes. Inorganic coatings in general tend to have poor mechanical properties, which results in film cracking and impaired barrier properties.[12,45-49] This is a drawback in many applications.

The abrasion resistance of PLA with 25 nm Al_2O_3 was evaluated. Both Taber and Wallace tests were used. In Taber test, the rubber roll without extra loading was used. The deposition temperatures were 50, 80 and 100 ºC. Both tests had a dramatic effect on the polymer films (Table 6). The results indicated that a higher deposition temperature is favourable. It is obvious that a thin oxide layer has to be protected somehow from the abrasive stresses.

Table 6
OTR of PLA film with 25 nm Al_2O_3 after abrasive testing

OTRs, $cm^3/m^2/10^5$ Pa/d				
Al_2O_3 deposited at	Before abrasion	Taber abraser; rubber disc	Wallace abraser; Al_2O_3 against Al_2O_3	
		100 cycles	20 cycles	50 cycles
50 °C	1.3	150		260
80 °C	1.1	120	190	210
100 °C	1	91	96	130

Note: OTR of plain PLA film without Al_2O_3 layer exceeded 400 $cm^3/m^2/10^5$ Pa/d

Figure 5: Effect of uniaxial straining on the oxygen barrier of PLA with different thin films (left), and hardness of the same films on silicon wafer measured by nanointendation (right); (Further details can be found elsewhere[12,34])

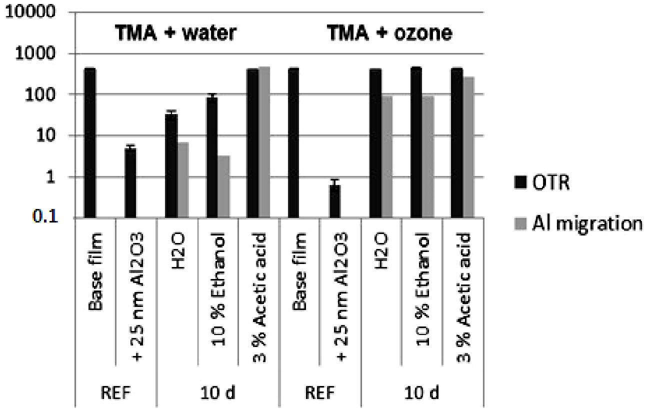

Figure 6: Effect of 10 days food simulant exposure on OTR ($cm^3/m^2/10^5$ Pa/d) and Al migration (µg/dm^2) of PLA film with 25 nm Al_2O_3

The flexibility of Al_2O_3 layers was improved by creating five-layer laminates based on alternating layers of Al_2O_3 and inorganic–organic aluminium alkoxide (alucone).[12] The flexibility of the polymer films with the thin layers was evaluated by uniaxial straining followed by barrier analyses and SEM imaging. Defects are not likely to occur in all the sublayers 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 – laminates showed improved flexibility compared to Al_2O_3 layers (Figure 5). Not surprisingly, the laminates having the highest total thickness of Al_2O_3 provided the best overall barriers before straining.

Flexibility 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. The WVTR depended more on the overall film properties, such as layer thickness and chemistry.
Nanoindentation tests on different thin layers and laminates deposited on silicon wafer indicated that the inorganic-organic hybrid also decreased the hardness of the thin layers (Figure 5).

Migration, compliance for food contact and occupational safety

ALD Al_2O_3 layers on PLA were exposed to food simulants in order to study the changes in the layer properties and the possible migration of Al to the food simulants. The migration of Al was small when the film was exposed to water and ethanol (Figure 6). 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. The migration of Al was higher when ozone was used as the oxygen source. Results with BOPP can be found elsewhere.[34,50]

In Plastics Regulation, specific migration limits are given for some authorized substances. According to Plastics Regulation, Al_2O_3 is allowed for manufacturing of plastic FCMs as an additive or a polymer production aid without specific restrictions.[30] However, for the authorized substances without specific migration limit or other restriction a generic migration limit (60 mg/kg food) is given. In setting the migration limits, authorities generally assess that 1 kg food is packed in a cubic box of 6 dm^2 surface area, leading also the requirement that the plastic materials should not transfer their constituents to food in quantities exceeding 10 mg/dm^2 of food contact surface. For non-authorized substances, a migration limit of 0.01 mg/kg food, corresponding to 0.0017 mg/dm^2, is set. The migration of Al exceeded this limit, but more importantly it was clearly lower than the general limit of overall migration (10 mg/dm^2).

Effects on the oxygen barrier of the Al_2O_3 layer were studied before and after the exposure to the food simulants. Oxygen barrier was decreased due to the tendency of Al_2O_3 to dissolve in the simulants (Figure 6). The most negative effect was observed with the acid simulant and the least negative with water. Although some metal oxides are less sensitive to dissolution than Al_2O_3, it is obvious that such thin metal oxide films need an additional 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.

In EU, materials in nanoform are allowed today for FCMs only when authorized. In our opinion, a uniform ALD Al_2O_3 barrier layer grown from precursors that react and bond readily with the plastic films do not fall under the European Commission's definition of nanomaterial. Such a thin film should not be considered as nanomaterial although its thickness is in the nanoscale. Instead, it might be called a nanostructure. ALD layers resemble 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. The European Food Safety Authority (EFSA) has already evaluated the safety of a barrier nanocoating of SiO_2 formed on PET articles.[51] Nanosilica is one of the nanomaterials accepted for plastic FCM.

As far as occupational safety is concerned, metal-organic precursors are pyrophoric, flammable or react violently with water. They can cause skin corrosion and thus proper protective clothing and personal protective equipment are crucial. These chemicals have to be stored in closed metal containers and handled in oxygen free environment. Likewise, oxidizing precursors, such as ozone, and reaction products, such as hydrochloric acid, are hazardous. The entry of such compounds into the research environment has to be prevented. Mechanical risks 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 plastic 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.

Additional sealant and protective layers

Plastic films and coated paperboards with thin Al_2O_3 films are prone to various hazards, such as mechanical stresses during further converting and direct contact with liquids, as pointed out in this paper. In addition, inorganic thin films tend to impair in most cases the heat sealing properties. Therefore, a laminate structure with an additional plastic film or coating is likely the final material structure also for packaging applications. Such solutions are being studied intensively.

An additional protective and polymer sealing layer can be performed in a subsequent extrusion coating process. Adhesion of extrusion coated polymer layers on an ALD Al_2O_3 thin film has been investigated.[52] Here the base substrate was PET coated paper. Only LDPE provided good adhesion to the Al_2O_3 surface, while the poor adhesion between PET or PLA and the substrate was caused by the lack of chemical bonding between the materials. However, it is possible to create inorganic/organic hybrids on top of the metal oxide film by using an organic compound, such as lactic acid, as an oxidizing precursor instead of water or ozone. It has been shown that adhesion of PLA to an Al_2O_3 surface can be improved with a lactic acid/TMA hybrid.[16]

Extrusion coating of polymers with high melt temperatures at low coating speeds can have a detrimental effect on the temperature sensitive base polymer onto which the thin Al_2O_3 film has been deposited. Different thermal expansion between the layers or even downright melting of the base polymer can destroy the Al_2O_3 film, which also explains why in some cases two plastic films with Al_2O_3 layers can be heat sealed against each other.[17] In most cases, dry or solvent free lamination would actually be a more feasible process. This is also typically used for metalized and other metal oxide coated plastic films today with adhesive suppliers having special adhesives for such surfaces.

CONCLUSION

Thin aluminium oxide films deposited with ALD at low temperatures clearly improved the barrier properties of most substrates studied. A significant impact was observed with cellulose and polyester films, which indicated the importance of polar oxygen groups. However, additives such as antioxidants can prevent the growth of such thin films. Likewise, the polymer coatings on fibre-based webs have to be uniform and defect-free prior to the ALD.

Surface chemistry of polymer films has an impact on thin ALD layers. Therefore, it is no surprise that corona and plasma pretreatments can improve the barrier properties of thin layers. Likewise, the properties of thin films can be improved by prolonging the initial deposition cycle. However, it is important, as with polymer films to be e.g. metalized, to prevent the surface from attracting contaminants prior to the ALD.

The reactor temperature should be as high as possible and yet lower than the temperature at which the polymer degrades, melts or softens. However, a too low deposition temperature would require longer overall cycle times. The choice of oxygen source is an additional tool to affect the thin film properties, and ozone can be used to activate difficult polymer surfaces.

Proper mechanical properties are a key requirement for several packaging materials. Thin films have to be protected from mechanical stresses and contacts with liquids with an additional polymer layer also acting as a sealant. In addition, the mechanical and surface properties of thin layers can be adjusted by combining inorganic oxide and inorganic-organic hybrid layers.

ALD coated film should be considered as a plastic covered by an inorganic coating, although the thickness of the ALD layer is in the nanoscale. However, the legislation related to nanomaterials and its definition is in progress in the EU and should be followed carefully.

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