

Atomic Layer Deposition of Metal Oxide Films as Diffusion Barriers on Flexible Packaging Materials

T.O. Kääriäinen, P. Maydannik, and D.C. Cameron, ASTRaL, Lappeenranta University of Technology, Mikkeli, Finland; and K. Lahtinen, P. Johansson, and J. Kuusipalo, Paper Converting and Packaging Technology, Tampere University of Technology, Tampere, Finland

ABSTRACT

One of the most promising areas for the industrial application of atomic layer deposition (ALD) is gas diffusion barriers on polymer based materials. In this work a novel packaging material system with improved diffusion barrier properties has been developed. Nanometer scale metal oxide films have been applied to paper-based packaging materials and their diffusion barrier properties have been studied by means of water vapor and oxygen transmission rates. The paper is firstly extrusion coated with polymer film followed by ALD deposited Al_2O_3 . The polymers used as extrusion coatings were polypropylene, low and high density polyethylene, polylactide and polyethylene terephthalate. Water vapour transmission rates (WVTRs) were measured according to method SCAN-P 22:68 and oxygen transmission rates according to a standard ASTM D 3985. A 10 nm oxide layer already decreased the oxygen transmission by a factor of 10 compared to uncoated material. WVTR with 40 nm ALD layer was better than the level currently required for most common dry flexible packaging applications. When the oxide layer thickness was increased to 100 nm and above, the measured WVTRs were limited by the measurement set up. Using an ALD layer allowed the polymer thickness on flexible packaging materials to be reduced. Once the ALD layer was 40 nm thick, WVTRs did not improve with increasing polymer layer thickness. Thus, nanometer scale ALD oxide layers have been shown to be an effective way to fabricate flexible packaging materials with high quality barrier properties.

INTRODUCTION

In flexible packaging polymer extrusion coating has been the main technology to produce gas permeation barriers on fiber-based materials. The most commonly used polymers for such technology are high and low density polyethylene (HDPE, LDPE) and polypropylene (PP) [1, 2]. A very interesting and increasingly used group of polymers in extrusion coating is that of biodegradable polymers. They may have a great impact in sustainable development where the main challenges are the solid waste management and the reduction of usage of petrochemical sources [1]. Specifically, polylactides (PLA) have also been studied for their ability to meet the requirements of flexible packaging applications [3]. Polylactides and polyglycolic acids (PGA) have also wide application in medicine and surgery due to their biocompatibility [1]. One

drawback of the polymer-coated fiber-based materials still is that they do not meet all the demands of barrier performance in flexible packaging applications today. The demands are dependent on varying climatic and transportation conditions but also by the requirement to reduce the polymer coating weight because of technical and commercial disadvantages (curling, material, costs etc.) [4].

The gas permeation through a single inorganic layer is dominated by the defect size and density in the film [5-7]. The development of inorganic layer based ultrabarriers has concentrated e.g. on multilayer structures [8, 9], modification of inorganic layer chemical structure [10] and single layer optimization [11-13]. Atomic layer deposition (ALD) has been shown to be a versatile thin film deposition method to fabricate high performance diffusion barriers on polymer films [11-13]. For PEN and Kapton® substrates Groner et.al. reported 5 nm Al_2O_3 ALD film to possess oxygen transmission rates (O_2TR) lower than $5 \times 10^{-3} \text{ cm}^3/\text{m}^2/\text{day}$ at 23°C and 50% relative humidity (RH) and 26 nm Al_2O_3 ALD film to have WVTR of $\sim 1 \times 10^{-3} \text{ g}/\text{m}^2/\text{day}$ [11]. Depending on the test method used even lower water vapor transmission rates (WVTR) of $\sim 6 \times 10^{-6} \text{ g}/\text{m}^2/\text{day}$ have been reported with 25 nm Al_2O_3 layers on PEN substrates suitable for organic light-emitting diode (OLED) devices [12]. The main advantages of ALD are the extreme degree of conformality and uniformity which can be obtained even on complex-shaped structures [14]. As a chemical vapor deposition method ALD is favorable over the physical methods such as sputtering that can be detrimental to the polymer surface. In this paper the potential of ALD on flexible fibre-based packaging materials will be demonstrated. The water and oxygen permeation through a variety of polymer extrusion coated paper can be significantly decreased by adding an Al_2O_3 ALD film.

EXPERIMENTAL

Atomic layer deposition

Al_2O_3 was deposited on polymer extrusion coated paper materials at low temperatures ranging from 65°C to 150°C by atomic layer deposition (ALD) using a Beneq TFS-500 ALD tool. The polymer extrusion coated paper samples were prepared at the pilot paper converting line of the Paper Converting and Packaging Technology of Tampere University of Technology. The coating polymers chosen for the trials were LDPE (CA7230, Borealis), PP (WF420HMS,

Borealis), PET (Lighter C98, Equipolymers) and PLA (test grade). Different polymers were chosen to cover the diversity in heat resistance and surface properties. LDPE-coated paper was used in the combination of the polymer and inorganic ALD layer. Three different polymer coating weights, 18, 27, and 36 g/m², were used for LDPE to study the effect of the polymer layer thickness on diffusion barrier properties. Other polymers were studied only by using 25 g/m² coating weight. The ALD film thickness was varied between 10 nm and 200 nm. Depositions were performed only on the polymer coated side of the paper.

Film and substrate surface characterization

ALD film thickness was measured from silicon (100) substrates by using spectroscopic ellipsometry (J.A.Woollam Co., Inc. M-2000FI). The surface morphology of the polymer extrusion coated papers with and without the ALD film was examined by tapping-mode atomic force microscopy (AFM) (CP-II Scanning Probe Microscope, Veeco Instruments).

Diffusion barrier performance measurements

The diffusion barrier properties were tested by means of the water vapor transmission rate (WVTR) and oxygen transmission rate (O₂TR). The test procedure for WVTR followed the SCAN P22:68 (cup method). The WVTRs were measured in two atmospheric conditions: 23°C, 50% RH and 38°C, 90% RH. The O₂TR measurements were done with Mocon Ox-Tran Model 2/21 according to a standard ASTM D 3985. The conditions used for O₂TRs were 23°C, 0% RH.

RESULTS AND DISCUSSION

Barrier properties

In Figure 1 the WVTRs measured at 38°C and 90% RH with three different LDPE coating thicknesses as a function of ALD film thickness are shown. Below the ALD film thickness of 16 nm the WVTR only slightly decreases. A significant decrease in WVTR can be achieved with ALD film thickness of around 30 nm. When the ALD film thickness is further increased considerable reduction of WVTR can still be seen and the polymer coating weight becomes of less importance. The decrease in WVTR after 16 nm ALD film thickness is attributed to the existence of more defect free and uniform ALD film structure leading to a more efficient barrier. Increasing the ALD film thickness to the level of around 100 nm on LDPE does not really improve the barrier performance anymore, as shown in Figure 3. This behavior suggests that above this certain film thickness, ALD film on this type of flexible material is more susceptible to exterior effects and consequently the barrier properties are dominated by these defects rather than other diffusion effects.

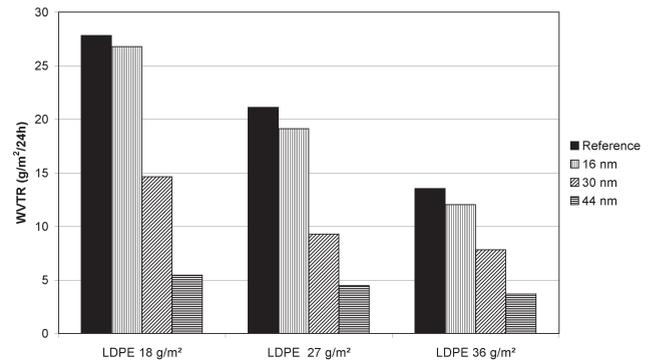


Figure 1: WVTRs (38°C, 90% RH) of bare LDPE and 16, 30 and 44 nm Al₂O₃ deposited LDPE. ALD growth temperature was 65°C.

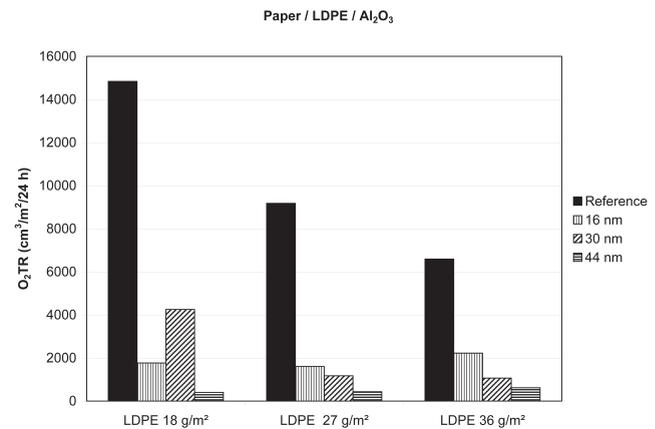


Figure 2: O₂TRs (23°C, 0% RH) of bare LDPE and 16, 30 and 44 nm Al₂O₃ deposited LDPE. ALD growth temperature was 65°C.

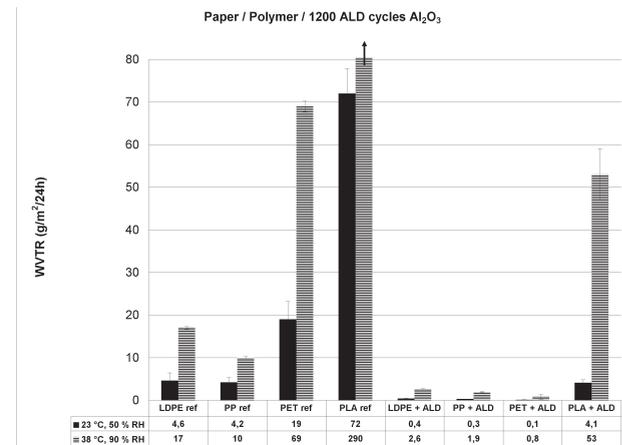


Figure 3: WVTRs (38°C, 90% RH and 23°C, 50% RH) of bare LDPE, PP, PET and PLA, and 1200 ALD Al₂O₃ cycles deposited LDPE, PP, PET and PLA. ALD growth temperature was 65°C. Film thickness ~100 nm.

Differences in behavior of ALD films can be observed in the barrier properties against oxygen and against water as shown in Figure 2. Already 15 nm Al_2O_3 gives considerably lower O_2TR compared to reference material. This behavior is attributed to the fact that the initial O_2TR of LDPE is quite high while its WVTR is low and the effect of ALD film on the barrier is more apparent in the case of oxygen permeation. After the initial growth of ALD film, the level of O_2TR remains at the same level regardless of polymer coating weight. Thus it can be concluded that the oxygen barrier performance in this type of barrier system is ALD film dominated.

The significant decrease in O_2TR already with around 16 nm ALD film shown in Figure 2 suggests conformal film structure, since the oxygen diffusion through the inorganic film has been reported to be mainly dominated by the defects and micron-scale pinholes in the film [21]. In Figure 4 the O_2TR s of around 100 nm Al_2O_3 are shown. It can be seen that increasing the ALD film thickness from around 40 nm to 100 nm does not significantly improve the barrier performance. As suggested before, a possible reason for this may be the defects generated in the ALD film. The anomalous increase in O_2TR for 18 g/m² polymer coating with 30 nm ALD film shown in Figure 2 may be due to defect formation during the sample handling and is also good indication of the sensitivity of nanometer-scale film to external effects.

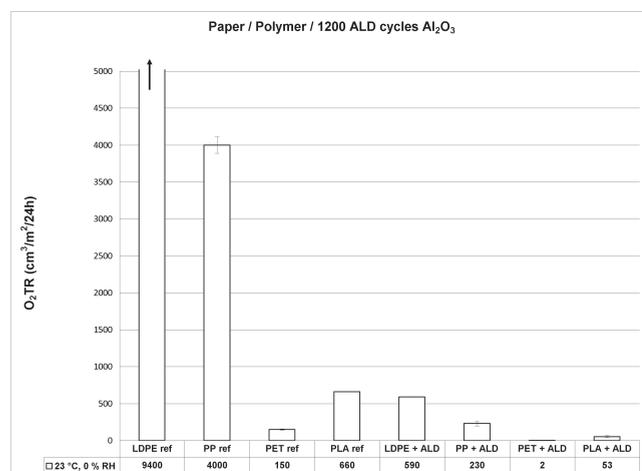


Figure 4: O_2TR s (23°C, 0% RH) of bare LDPE, PP, PET and PLA, and 1200 ALD Al_2O_3 cycles deposited LDPE, PP, PET and PLA. ALD growth temperature was 65°C. Film thickness ~100 nm

The results of WVTR and O_2TR measurements for the films over 100 nm thickness deposited at 65°C on LDPE, PP, PET and PLA are shown in Figures 3 and 4 respectively. In the case of WVTR it is critical to notice that the measurement conditions have a major effect on transmission rates. For the LDPE, PP and PET with ALD film thickness of around 100 nm, the WVTRs at 23°C and 50% RH show a level below

1 g/m²/24h, while at 38°C and 90% RH the WVTRs remain at higher levels except for PET, which shows a value below 1 g/m²/24h. The barrier performance of PLA can be clearly improved with around 100 nm ALD Al_2O_3 film but the WVTR still remain at moderate level.

The oxygen barrier properties of polymer extrusion coated paper materials shown in Figure 4 reveal the difference between the polymers both in O_2TR levels and in the barrier system behavior. Initial O_2TR s for these four different polymers show quite extensive variation. Also the relative decrease in O_2TR with the ALD film added shows variation between the polymers. The relative decrease in O_2TR with the Al_2O_3 film of 1200 ALD cycles is highest for the PET and lowest for the PLA. These variations are attributed to the differences in both polymer bulk and surface structure. The lowest O_2TR and WVTR of Al_2O_3 deposited PET suggest that PET is favorable substrate for ALD film deposition for further improvement of the diffusion barrier properties. This can be explained by, for example, PET having a lower density and size of surface defects.

Bare LDPE and PP show relatively low WVTRs, while the WVTR of bare PET and PLA remains clearly higher level. Although the highest decrease in both WVTR and O_2TR with 1200 ALD cycles Al_2O_3 film can be seen for PET which indicating that LDPE, PP and PLA have higher effect on permeation rates in the combined barrier system than PET. This gives reason to believe that in the development of barrier performance where a thin nanometer-scale inorganic layer is combined with polymer film, it is essential to concentrate on the structural characteristics of the polymer, particularly reduction of irregularities on the polymer surface. Furthermore it is important to notice the actual permeation rates of the barrier system since they define the material usability in the final barrier application. For example the WVTR of all the polymers with around 100 nm ALD film, instead of PLA, meets the requirements for dry packaging solutions, but the ambient temperature in the final application may define the polymer chosen for the barrier structure.

Surface morphology

PP and PET were chosen here to illustrate the difference in polymer surface morphology. AFM images of 100 μm^2 in Figure 5 show that the both of the surfaces are structured by the features such as longitudinal cavities and dents that have been formed during the polymer extrusion process. In general Al_2O_3 ALD film seems to cover the polymer surfaces, based on the observation that the typical features of the uncoated polymer surface can be seen underneath the ALD layer in Figures 5a and 5b. Presumably ALD is applicable technique on these types of surfaces since it grows conformally in deep trench structures [5]. However, a closer look at the surface morphology in Figure 5c and 5d reveals the difference in behavior under the ALD process. The PET surface shown in

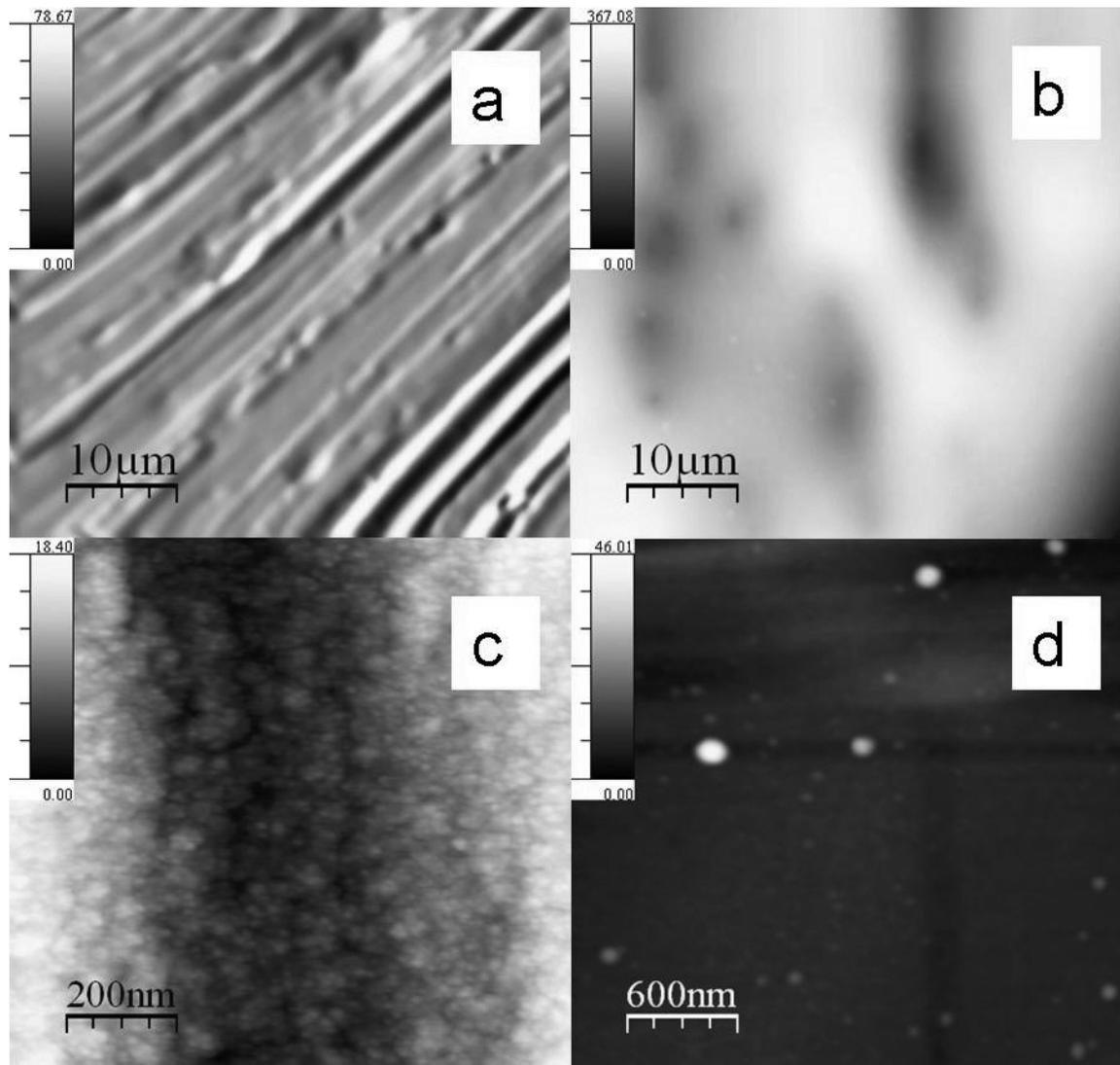


Figure 5: AFM images of Al_2O_3 deposited PP (a, c), and PET (b, d).

Figure 5d remain generally smooth except for round shaped granules attributed to PET crystallization. The PP surface after deposition appears more granular with voids as shown in Figure 5c. Even though both of these polymers undergo changes in their surface morphology during the ALD cycling, the changes in PET do not seem to have much affect on barrier performance compared with PP. The highest relative reduction in both WVTR and O_2TR was seen for PET. Furthermore, a good indication of the ability of the ALD to cover the nano-structured surface is also the relatively low transmission rates achieved for PET, even though the round shape granules are formed at the surface during the deposition. The voids in PP surface shown in Figure 5c are suggested to be possible pathways for gas diffusion.

CONCLUSION

Al_2O_3 was deposited by atomic layer deposition on LDPE, PP, PET and PLA extrusion coated paper materials. The results show significantly improved barrier properties against water and oxygen permeation. The WVTR and O_2TR measurements indicated that for Al_2O_3 deposited on LDPE extrusion coated paper, the barrier performance of the structure improved with increasing ALD film thickness up to a limit of around 100 nm.

Diffusion barrier performance of the barrier system combining polymer extrusion coating and inorganic ALD layer varies between different polymers. This is attributed to the presence of irregularities both in the ALD layer and the polymer film as

a consequence of different polymer chemical structure, surface morphology and behavior under thermal cycling. Over 100 nm Al_2O_3 film deposited on PET measured at tropical conditions of 38°C and 90% RH decreased WVTR below the level of 1 g/m²/day. On LDPE and PP with roughly the same ALD film thickness, WVTR around 2 g/m²/day was achieved. The relative decrease in WVTR and O_2 TR for PLA was in the same range with LDPE and PP, but the WVTR of Al_2O_3 deposited PLA remained at a moderate level, presumably because of a high defect level in the PLA. The results show that ALD is a technique applicable to improving the barrier performance of polymer extrusion coated flexible packaging materials which can meet the requirements of tropical conditions.

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