

Effect of Heat-Treatment on the Performance of Gas Barrier Layers Applied by Atomic Layer Deposition onto Polymer-Coated Paperboard

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ABSTRACT: The effect of heat treatment on the gas barrier of the polymer-coated board further coated with an Al₂O₃ layer by atomic layer deposition (ALD) was studied. Heat treatment below the melting point of the polymer followed by quenching at room temperature was used for the polylactide-coated board [B(PLA)], while over-the-melting-point treatment was utilized for the low-density polyethylene-coated board [B(PE)] followed by quenching at room temperature or in liquid nitrogen. Heat treatment of B(PLA) and B(PE) followed by quenching at room temperature improved the water vapor barrier. However, because of the changes in the polymer morphology,

quenching of B(PE) with liquid nitrogen impaired the same barrier. No improvement in oxygen barrier was observed explained by, e.g., the spherulitic structure of PLA and the discontinuities and possible short-chain amorphous material around the spherulites forming passages for oxygen molecules. This work emphasizes the importance of a homogeneous surface prior to the ALD growth Al₂O₃ barrier layer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2221–2227, 2011

Key words: barrier; gas permeation; morphology; nanolayers; thin films

INTRODUCTION

The trend today is to develop sustainable and light-weight packaging materials, which are not interfering with the energy and material recovery schemes set for the packaging waste. Traditional packaging materials typically consist of layers of oil-based polymers and aluminum foil, which are difficult to sort out and recycle efficiently. Simultaneously, there is an increasing interest to develop new kinds of renewable solutions, and this opens up new application areas for fiber-based materials and biopolymers. Polylactide (PLA) is a biopolymer that can be synthesized from renewable resources, and is thus, environmentally and economically appropriate.¹ Properties such as biodegradability and good mechanical strength make PLA interesting raw-material for many recyclable products. In addition, PLA is an attractive material option for the traditional applications where common thermoplastics, such as low-density polyethylene (LDPE) are employed. Like many other biopolymers, PLA loses barrier properties in high humidity conditions because of absorp-

tion of water and swelling of the polymer. Previously thin SiO_x coatings have been employed to improve the barrier properties of these sensitive materials.^{2,3} Various kinds of thin inorganic coatings are often utilized to create high performance materials, e.g., food packages.

Atomic layer deposition (ALD) technique is a surface controlled layer-by-layer thin film deposition process based on self-terminating gas-solid reactions. It allows preparation of dense and pinhole-free inorganic films that are uniform in thickness.⁴ In our previous work thin Al₂O₃ and SiO₂ coatings have been successfully deposited by the ALD technique at low temperatures on various polymer-coated papers, boards, and plain polymer films.^{5–7} The work demonstrated that ALD is a feasible deposition technique when making extremely thin (25 nm) barrier coatings from Al₂O₃ onto such temperature-sensitive fiber-based materials.⁶ Despite the promising results, improvement in barrier performance toward gases is needed to create barrier coatings suitable for demanding packaging purposes. One route toward improved barrier performance is to pretreat the substrate before the inorganic ALD coatings. In our earlier studies,⁷ corona pretreatment slightly enhanced the oxygen barrier performance of thin Al₂O₃ layers on LDPE-coated board.

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The effects of heat treatment on polyolefin-coated papers and PLA-coated boards have also been studied.^{8–10} Barrier properties of polymers are affected by the chemical structure, morphology, and surface properties.¹¹ In addition, the process used for forming the polymer influences the barrier properties. This is due to the redistributed crystalline and amorphous regions and the overall change in free volume of the polymer when the film is formed. To get good adhesion the polymer has to be applied at high melt temperatures followed by rapid quenching to avoid adhesion to the chill roll of the process equipment. This leads to a polymer layer with low density as molecules do not have time to pack efficiently. In extrusion coating, polymer crystallinity has been found to be inversely related to the difference between the melt temperature and the quenching temperature¹² leading sometimes to formation of a totally amorphous structure. This is the case with PLA coatings.^{8,10} Diffusion of gas permeants occurs through the amorphous regions, whereas crystalline regions are more or less impermeable. Water vapor transmission rate (WVTR) of PLA decreases with increasing crystallinity.¹³ This may be due to the fact that restricted amorphous regions have higher resistance to water vapor permeation compared with the free amorphous regions. Based on recent studies^{9,10} concerning PLA, the improved water vapor barrier after treatment at 130°C was due to the increase in crystallinity and the growth of spherulites.

Crystallization and formation of spherulites in polyethylenes have been studied elsewhere.^{14,15} In the work by Scheirs et al.¹⁵ the thermal oxidation during isothermal crystallization at 123°C decreased the size of the spherulites similarly to fast quenching. Short-chain material is usually deposited at the boundaries of the spherulites and edges of lamellae creating brittle areas. The over-melting-point heat treatment has also been shown to improve the barrier properties of polyethylene-coated paper.^{8,10} This was explained by increased level of crystallinity and spherulite size after quenching at room temperature. A dramatic improvement was observed in oxygen transmission rate after 5 min treatment at 210°C, while water vapor barrier was slightly impaired. Increased oxidation was accounted to be the reason for the increased water vapor permeation. The mobility of polymer chain is restricted in the crystalline region and also between such regions.¹⁶

The aim of this work was to study the effects of a heat treatment on the oxygen and water vapor barrier performance of polymer-coated boards additionally coated with a thin Al₂O₃ layer by the ALD technique. Our hypothesis was that an improvement achieved with such a heat treatment in an originally poor barrier property plays little role if the properties of the Al₂O₃ layer grown by the ALD technique

dominates. Indirectly the heat treatment could have significant effects on the surface chemistry and topography, and diffusion of ALD precursors into and out of the polymer.

EXPERIMENTAL

Commercial paperboards coated with synthetic LDPE (B(PE); board 210 g/m²; polymer coating 15 g/m²) and the same base board coated with bio-based PLA (B(PLA); coating 27 g/m²) were used as substrates for the Al₂O₃ depositions by ALD. Before the depositions the substrates were heat-treated in a convection oven. The test conditions were chosen based on the previous works.^{8–10} For B(PE) the temperature of the oven was 170°C or 200°C, and 130°C for B(PLA). For B(PE) the heat-treatment lasted for 5 min after which the samples were quenched at room temperature (23°C) or dipped into liquid nitrogen. With B(PLA) the treatment lasted for 4, 9, or 16 min followed by quenching at room temperature. The times used for inserting and removing the samples into and from the oven were approximately constant throughout the test series.

Plain and heat-treated substrates were coated with Al₂O₃ by ALD technique at 80°C using a commercial SUNALE™ R-series ALD reactor manufactured by Picosun Oy. The targeted coating thickness was 25 nm. The ALD procedure for the Al₂O₃ depositions has been reported elsewhere.^{6–7} The precursors used for the Al₂O₃ depositions were trimethylaluminum (TMA; SAFC Hitech, electronic grade purity) and water. High purity N₂ was used as a carrier and purge gas. The precursor pulses lasted 0.1 s and the purges 5 s. The resultant film growth rates and film thicknesses on the polymer-coated boards could not be directly measured. Instead, the coating thickness was produced according to the reactor process parameters and compared with the thickness of Al₂O₃ on a silicon wafer analyzed with a Nanospec AFT4150 reflectometer. Because of the different polarities and functional groups the growth rates on the polymer-coated boards may deviate from that determined with the silicon wafer.^{17,18}

Contact angle and surface energy measurements were performed both for plain and heat-treated substrates to detect possible chemical changes caused by the heat-treatment. The measurements were made with KSV CAM 200 Optical Contact Angle Meter in a controlled atmosphere (RH 50%, temperature 23°C) and were expressed as ° for contact angle and mN/m for surface energy. The probe liquids used were H₂O and di-iodomethane (CH₂I₂). Results are given as an average of three to eight parallel measurements. The surface energy values, including dispersive and polar components, were calculated from the contact angle data using the OWRK (ext.

Fowles) theory. Contact angle values were measured at the time of 1 s from the moment the drop contacts the surface.

Atomic force microscopy (AFM tapping mode; Park Systems XE-100 with 905-ACTA cantilever) was used to study the surface topography and morphology of plain and heat-treated substrates to detect changes caused by the heat-treatment. From each sample three parallel sample areas of $5 \times 5 \mu\text{m}$ and $0.5 \times 0.5 \mu\text{m}$ were analyzed. In addition the values of average roughness (R_a) and root mean square roughness (R_q) were calculated from the larger area images. Both topography and phase images were taken. The phase lag is partially a function of the viscoelastic properties of the sample surface.¹⁹

Wide-angle x-ray scattering (WAXS) was measured from the samples in perpendicular transmission geometry to observe the morphological changes caused by the heat-treatment. The radiation was produced with a rotating anode X-ray generator using Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) monochromatized with a Si(111) crystal and a totally reflecting mirror. An image plate detector (MAR345, Marresearch) was used to detect the scattered radiation in perpendicular transmission geometry. Additionally, the air scattering with an empty sample holder and the "dark current" without beam were measured. These, as well as corrections due to the measurement geometry, measurement time, and absorption were considered during the analysis. The measured q -range was 0.3–3.1 $1/\text{\AA}$ with the definition $q = (4\pi \sin \theta)/\lambda$ for the length of the scattering vector.

Water vapor and oxygen transmission rates were measured from untreated and heat treated samples with and without the ALD- Al_2O_3 layer. The water vapor transmission rate (WVTR) was measured from three to five parallel flat samples according to the modified gravimetric methods ISO 2528 : 1995 and SCAN P 22 : 68, and was expressed as $\text{g}/\text{m}^2/\text{day}$. Test conditions were 23°C and 75% relative humidity. The oxygen transmission rate (OTR) was measured from two to eight parallel samples using humid gases at room temperature (23°C, 50% relative humidity) with Systech M8001 and expressed as $\text{cm}^3/\text{m}^2/10^5 \text{ Pa}/\text{day}$.

RESULTS AND DISCUSSION

Surface topography and polymer morphology

The results from the surface topography and morphology measurements are presented in Table I. The effect of heat-treatment on B(PE) was obvious. The plain substrate was rough as indicated by the high R_a and R_q values, and the large deviation between the measured areas. The smoothest B(PE) sample was heat treated at 200°C followed by quenching with

TABLE I
Average Roughness (R_a) and Root Mean Square Roughness (R_q), Both in nm, Obtained from Three Parallel Surface AFM images (area $5 \times 5 \mu\text{m}$)

Sample	R_a	R_q
B(PE)	68 ± 42	89 ± 58
B(PE), 170°C, RT	16 ± 2.4	20 ± 3.4
B(PE), 200°C, RT	20 ± 8.3	26 ± 11
B(PE), 170°C, LN	18 ± 5.4	22 ± 7.2
B(PE), 200°C, LN	13 ± 1.4	17 ± 1.7
B(PLA)	110 ± 63	137 ± 70
B(PLA), 4 min 130°C	27 ± 11	34 ± 18
B(PLA), 9 min 130°C	28 ± 21	35 ± 18
B(PLA), 16 min 130°C	26 ± 11	34 ± 15

RT refers to quenching at room temperature, LN to quenching with liquid nitrogen.

liquid nitrogen. However, taking into account the statistical scattering, all the heat-treated B(PE) samples were similar. Plain B(PLA) was rougher than the commercial PLA-coated board in our previous studies^{5–7} and the B(PE) used. Heat-treatment decreased the surface roughness, and with the longer treatment time the roughness of the surface became more uniform. The heat-treated B(PLA) samples were rougher than the heat treated B(PE) samples. However, in the case of B(PE), surfaces revealed that the amount of small scale surface features actually increased as a result of the heat-treatment. The phase images indicated more organized structures with the samples quenched at room temperature than those quenched with liquid nitrogen. This is shown in Figure 1. With B(PLA) the effect was significant which can be seen in Figure 2. The amount of spherulites increased with increased treatment time in the oven. High crystallinity of samples heat-treated for 9 and 16 min seemed also to create discontinuation points between the spherulites (Fig. 3).

When determining the crystal sizes and crystallinities of cellulose by WAXS, the measured scattering of sulfate lignin was used to approximate the amorphous background of cellulose.²⁰ The intensity pattern was integrated on a sector of 180° in the plane of the image plate. For the crystal size determination, the amorphous background was subtracted and the size was calculated with the Scherrer equation²¹ after fitting Gaussian functions to the diffraction peaks. This was possible for the 200-reflection of cellulose (1.6 1/\AA) in the B(PLA) samples only, because the diffraction peaks of LDPE in B(PE) could not be separated from the cellulose peaks. According to the results, the crystal size of cellulose in 200-direction (crystal width) was increased from 53 Å to 60 Å due to heat-treatment of B(PLA) samples, being 48 Å for an uncoated paperboard ($\pm 1 \text{ \AA}$ for all). The crystallinity of cellulose was determined for the reference sample and the plain B(PLA) substrate by fitting 24 Gaussian functions corresponding to the theoretical

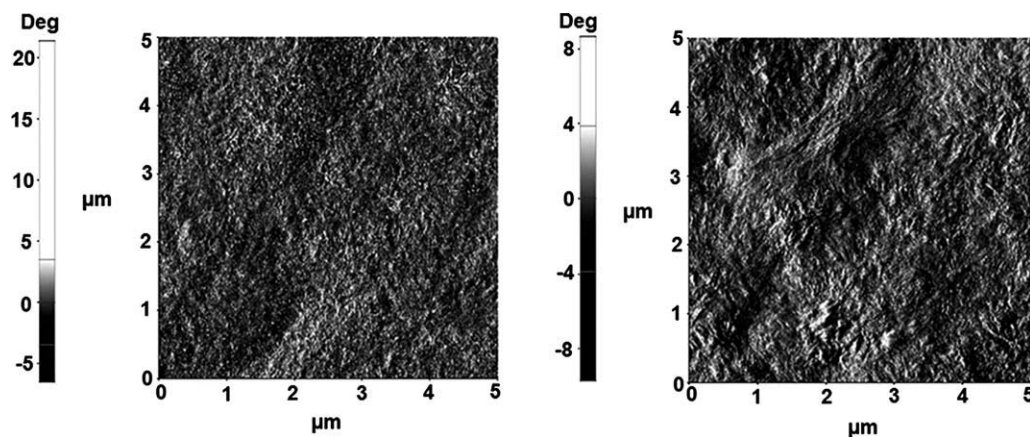


Figure 1 Phase AFM images of LDPE surfaces after 5 min heat-treatment followed by quenching with liquid nitrogen (a) and quenching at room temperature (b).

reflections of cellulose I β ²² in the data and calculating the ratio of the measured intensity and the approximation for the amorphous background. No significant difference was observed between the two samples.

The order parameter²³ describing the orientation of cellulose crystals with respect to the machine direction was calculated from the two-dimensional WAXS patterns of all samples. A narrow radial range at the peak of the 200-reflection of cellulose was chosen to minimize the contribution of the peaks of PLA and LDPE. This parameter describes

orientational order in the samples and has a value of 0 for no orientation and a value of 1 for fully oriented samples. Orientation of cellulose crystals in the machine direction (direction the web runs on board machine) was observed in all samples, with order parameters varying in the range 0.03–0.05.

Heat-treatment of the B(PLA) samples increased the level of crystallinity in PLA gradually when comparing the intensity of the sharpest peak of PLA (020-reflection at $q = 1.18 \text{ 1/\AA}^{24,25}$) obtained from the heat-treated samples to the peak of the plain B(PLA) sample (Fig. 4). This is in agreement with

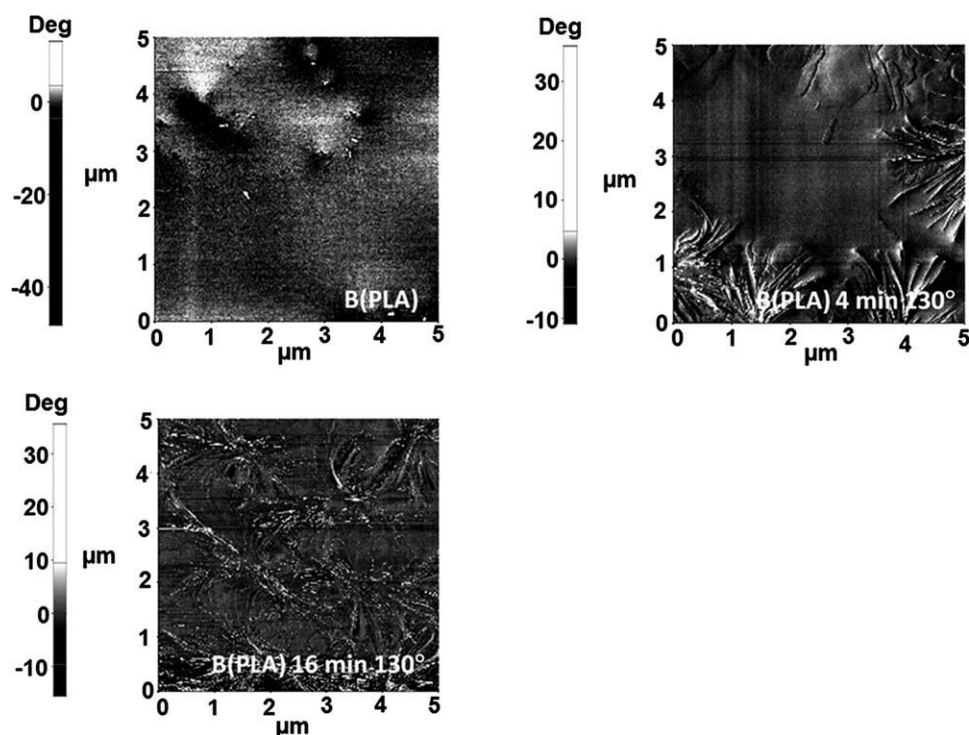


Figure 2 Phase AFM images of plain B(PLA) and B(PLA) after 4 and 16 min heat-treatment followed by quenching at room temperature.

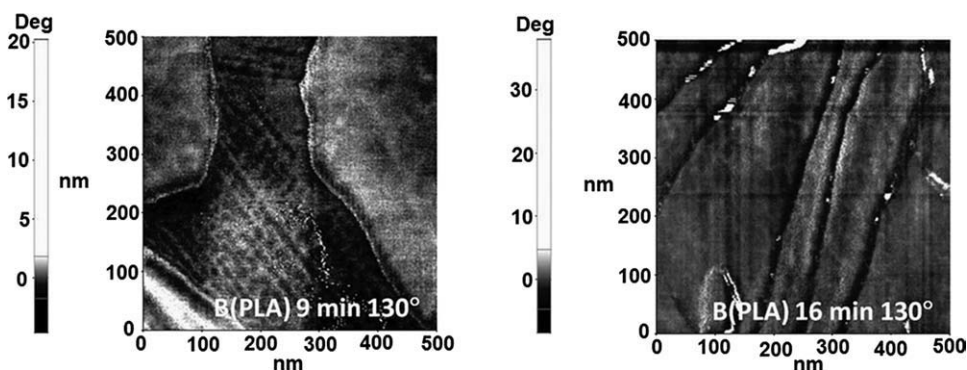


Figure 3 Phase AFM images of B(PLA) after 9 and 16 min heat-treatment followed by quenching at room temperature.

the observations from the AFM studies. The three other peaks in Figure 4 are the 101-, 023-, and 121-reflections of PLA, visible at $q = 1.05 \text{ 1/\AA}$, $q = 1.35 \text{ 1/\AA}$ and 1.58 1/\AA , respectively.^{24,25}

B(PE) samples were more challenging to analyze with WAXS due to the reason stated above. However, qualitative analysis of the data showing in Figure 5 was possible. The only diffraction peak of LDPE visible despite the cellulose background (110-reflection) is located approximately at $q = 1.52 \text{ 1/\AA}$. On the basis of visibility of this peak, it seems that plain B(PE) had the lowest crystallinity followed by B(PE) heat-treated at 200°C and the quenching with liquid nitrogen. B(PE) sample after similar heat treatment but slower quenching rate resulted in higher crystallinity. Samples heat-treated at 170°C where more crystalline regardless of the quenching process. It has to be kept in mind that more branched LDPE has lower crystallization tendency than HDPE or linear LDPE often used in such studies.

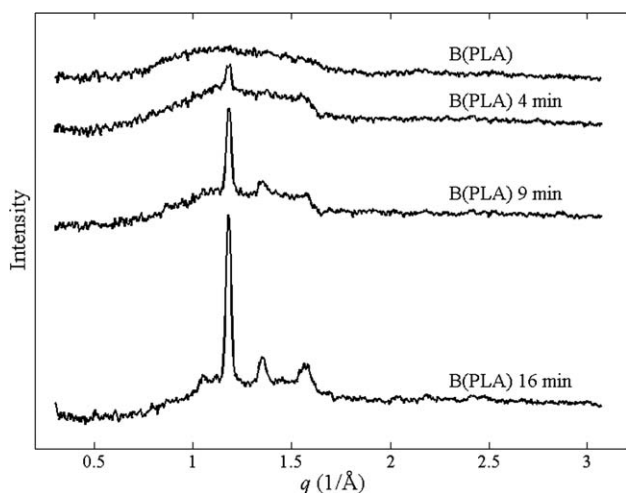


Figure 4 WAXS patterns from the plain and heat treated B(PLA) samples. The data for the uncoated reference board was subtracted from the curves.

Effect of heat-treatment on surface chemistry

Table II presents the results from the contact angle and surface energy measurements for the plain and heat-treated substrates. In the B(PLA) samples the hydrophobicity increased after 4 and 9 min of heat treatment at 130°C and then decreased after 16 min of heat treatment. This behavior can be explained by the surfaces containing both amorphous and crystalline regions, and the effect of such heterogeneity on apparent contact angles. After 16 min of heat treatment at 130°C the surface was covered with spherulites resulting in a slightly more hydrophobic surface compared with the amorphous surface. The values for the B(PE) samples were more constant. The samples which were heat-treated and quenched at room temperature had higher standard deviation in the contact angle values. These results support our findings from AFM and WAXS results. The scattering in contact angle makes also the analyses of the surface energy values based on the average contact angles difficult.

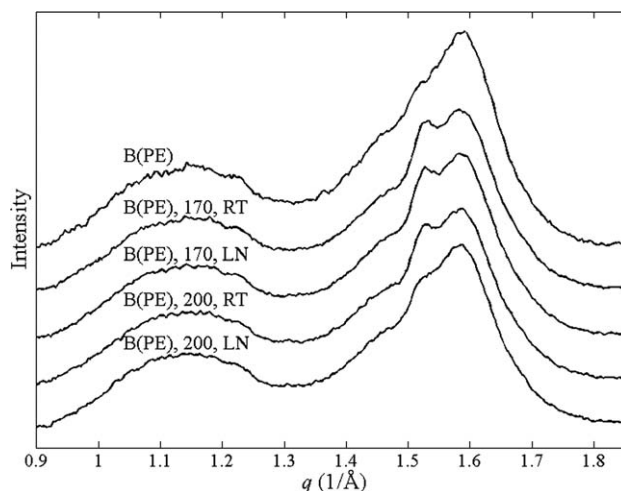


Figure 5 WAXS pattern of the plain and heat-treated B(PE) samples.

TABLE II

Average Contact Angles (°) of the Samples with Water and Di-iodomethane (DIM) from Three to Eight Parallel Measurements, and Surface Energies γ (mN/m) and Relative Polarity γ_p/γ Calculated from the Contact Angle Data Using the OWRK (ext. Fowles) Theory

Sample	Contact angle, H ₂ O	Contact angle, DIM	γ	γ_p/γ
B(PE)	85 ± 5.0	56 ± 1.8	34	11
B(PE), 170°C, RT	84 ± 13	60 ± 2.9	33	13
B(PE), 200°C, RT	96 ± 8.4	56 ± 2.3	32	2.7
B(PE), 170°C, LN	85 ± 1.9	57 ± 1.9	34	11
B(PE), 200°C, LN	90 ± 2.7	56 ± 0.7	33	6.8
B(PLA)	76 ± 2.2	37 ± 7.8	46	9.8
B(PLA), 4 min 130°C	99 ± 3.3	34 ± 1.0	42	0
B(PLA), 9 min 130°C	91 ± 9.5	65 ± 7.6	29	10
B(PLA), 16 min 130°C	80 ± 6.8	36 ± 2.0	45	7.1

The values of contact angles were measured one second after the initial contact between the sample surface and the test liquid. RT refers to quenching at room temperature, LN to quenching with liquid nitrogen.

Effect of Al₂O₃ coating on gas barrier properties of heat-treated substrates

Results from the barrier tests are presented in Tables III and IV. The water vapor barrier property of B(PE) was improved by the heat-treatment followed by quenching at room temperature. This can be explained by the increased crystallinity of LDPE. These results are similar to previous results reported.^{8,10} However, quenching of the heat-treated B(PE) with liquid nitrogen resulted in impaired water vapor barrier property. This is probably due to more amorphous structure when compared with the other samples.

The Al₂O₃ layer improved the oxygen and water vapor barrier properties of B(PE) and B(PLA) as such. In our previous studies^{5,6} increasing the thickness of the Al₂O₃ layer further from 25 nm was

TABLE III

Water Vapor Transmission Rates (g/m²/day) of Plain B(PE) and B(PLA) Substrates and Al₂O₃ Coated Substrates With and Without the Heat Treatment

Sample	Without ALD-Al ₂ O ₃	With ALD-Al ₂ O ₃
B(PE)	11 ± 0.6	1.7 ± 0.2
B(PE), 170°C, RT	7.6 ± 0.8	4.3 ± 3.6
B(PE), 200°C, RT	7.0 ± 0.2	3.7 ± 2.8
B(PE), 170°C, LN	15 ± 3.3	9.2 ± 5.3
B(PE), 200°C, LN	20 ± 6.6	5.8 ± 1
B(PLA)	98 ± 2.4	5.8 ± 2.3
B(PLA), 4 min 130°C	88 ± 1.7	3.0 ± 1.9
B(PLA), 9 min 130°C	78 ± 5.8	3.2 ± 0.8
B(PLA), 16 min 130°C	76 ± 6.8	11 ± 2.3

Two to eight parallel measurements were performed. The results are given as average ± standard deviation. Target thickness of Al₂O₃ layer was 25 nm. RT refers to quenching at room temperature, LN to quenching with liquid nitrogen.

TABLE IV

Oxygen Transmission Rates (cm³/m²/10⁵ Pa/day) of Plain B(PE) and B(PLA) Substrates and Al₂O₃ Coated Substrates With and Without of Heat Treatment

Sample	Without ALD-Al ₂ O ₃	With ALD-Al ₂ O ₃
B(PE)	7200 ± 3000	450 ± 90
B(PE), 170°C, RT	4600 ± 1300	8200 ± 3700
B(PE), 200°C, RT	85,000 ± 35,000	9200 ± 1200
B(PE), 170°C, LN	71,000 ± 41,000	9200 ± 2800
B(PE), 200°C, LN	>170,000	38,000 ± 14,000
B(PLA)	530 ± 35	120 ± 100
B(PLA), 4 min 130°C	650 ± 20	40 ± 23
B(PLA), 9 min 130°C	3400 ± 2300	>175,000
B(PLA), 16 min 130°C	7500 ± 70	>200,000

Two to eight parallel measurements were performed. The results are given as average ± standard deviation. Target thickness of Al₂O₃ layer was 25 nm. RT refers to quenching at room temperature, LN to quenching with liquid nitrogen.

needed to significantly improve the barrier properties of B(PE). In this study the improvement was obvious already with a 25 nm layer of Al₂O₃. The improvement was clear even when we used lower deposition temperature than previously. However, after the Al₂O₃ coating the WVTR values of the plain and the heat-treated B(PE) samples quenched at room temperature were on the same level, whereas the improvement in the water vapor barrier was not necessarily as unambiguous with the amorphous B(PE) samples that can be explained by the increased thermal mobility of the amorphous polymer chains. This makes the nucleation and growth of the Al₂O₃ layer more challenging leading to poor film formation or internal/interfacial stresses. In addition, oxidation of the amorphous polymer could impair the water vapor barrier performance. Heat treatment of B(PLA) also improved the WVTR, and the longer the heat-treatment the lower the WVTR. This is in agreement with previous studies.^{9,10,13} In the previous studies with B(PLA)^{5,6} the optimal Al₂O₃ layer thickness was 25 nm. With thicker Al₂O₃ layers (e.g., 50 nm and 100 nm) the barrier properties were impaired. However, the B(PLA) samples coated with the Al₂O₃ layer were similar to each other within the limitations of the test method. This indicates that the Al₂O₃ layer made by the ALD technique dominated the water vapor barrier properties.

The oxygen barrier property of B(PE) was little affected by the over-melt-point heat treatment at 170°C or at 200°C. The oxygen barrier property was impaired as temperature was increased or when quenching with liquid nitrogen was used due to a more amorphous LDPE coating. The reason for increased oxygen transmission rate after treatment at 200°C followed by quenching at room temperature could be the formation of pathways to permeants between the crystals along

the oxidized short-chain amorphous regions. Such a structure has been suggested earlier¹⁵—although for linear high-density polyethylene (HDPE). This finding of increased oxygen permeability is in disagreement with the results from others.^{8,10} In addition to different polyethylene used in these studies, one cannot rule out the effect of the base substrate which was in our case a rough paperboard. The best oxygen barrier was achieved when plain B(PE) was coated with the Al₂O₃ layer. The oxygen barrier properties with the Al₂O₃ layer were similar for the heat-treated samples quenched at room temperature and the sample heat-treated at 170°C followed by quenching with liquid nitrogen. The samples exposed to 200°C and quenched with liquid nitrogen exhibited the highest oxygen transmission rates both with and without the Al₂O₃ layer. This is in agreement with the water vapor barrier results.

In the case of B(PLA) a short heat treatment below the melting point had only a small effect on the oxygen barrier. The values were similar to the samples with the Al₂O₃ layer. However, as the heat-treatment at 130°C is prolonged to 9 or 16 min the increased crystallinity and the growing spherulites force the short-chain material with low crystallization tendency to the spherulite boundaries, as suggested for HDPE.¹⁵ If a PLA-based blend is used the different blend components might separate. Such areas had probably different response to the ALD process conditions, and the ALD layer uniformity was impaired thus creating additional pathways for oxygen molecules. In addition, oxygen barrier is more sensitive to resulting coating defects than water vapor barrier.

CONCLUSIONS

Heat-treatment of PLA-coated paperboard at 130°C and LDPE-coated paperboard at 170°C or 200°C followed by quenching at room temperature were found to be beneficial for the water vapor barrier performance. Quenching of LDPE-coated board with liquid nitrogen mainly increased the WVTR value, which was explained by changes in the polymer morphology. No systematic improvement in oxygen barrier property was observed which was explained by the spherulitic structure of PLA, and the discontinuities and low-chain material around the spherulites forming passages for oxygen molecules. An Al₂O₃ layer grown by the ALD technique improved the barrier properties of PLA and LDPE-coated substrates as such. However, heat-treatment of these substrates before applying the Al₂O₃ layer provided little or no practical means to improve the barrier performance. On the contrary, radical changes in the polymer morphology eventually impaired the barrier properties, and the thin Al₂O₃ layer could not in all

cases compensate for such changes in the substrate, probably due to an uneven nucleation and film growth and high mobility of amorphous LDPE and interspherulitic PLA chains. This indicates the importance of homogeneous surface before the Al₂O₃ coating. It was also observed that decreasing the ALD-Al₂O₃ deposition temperature from 100 to 80°C improved the barrier properties obtained with LDPE-coated board.

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