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Citation Surface and Coatings Technology vol. 205(2011):21-22, pp. 5088-5092

Date 2011

URL <http://dx.doi.org/10.1016/j.surfcoat.2011.05.017>

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Thin Al₂O₃ barrier coatings onto temperature-sensitive packaging materials by atomic layer deposition

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Abstract

Thin (25 nm) and highly uniform Al₂O₃ coatings have been deposited at relatively low temperature of 80 and 100 °C onto various bio-based polymeric materials employing the atomic layer deposition (ALD) technique. The work demonstrates that the ALD-grown Al₂O₃ coating significantly enhances the oxygen and water vapor barrier performance of these materials. Promising barrier properties were revealed for polylactide-coated board, hemicellulose-coated board as well as various biopolymer (polylactide, pectin and nano-fibrillated cellulose) films.

Keywords: Atomic layer deposition, Barrier, Packaging material, Recyclability, Aluminum oxide, Biopolymer

1. Introduction

Growing environmental concerns related to the use of synthetic polymers in the packaging industry have led to the need for new, especially bio-based, materials in such applications [1]. Currently synthetic polymers are widely used in packaging applications because of their relatively low cost and high performance. Bio-based packaging materials would have many advantages over their plastic competitors, such as sustainability and recyclability [2]. However, the sensitivity towards moisture restricts their extended use. One way to improve the water-sensitivity is to apply a surface coating.

“Barrier property” refers to a material’s capability to resist the diffusion of a specific species (molecule, atom or ion) into and through the material. To be a good gas and vapor barrier, the material needs to be pore-free. When considering polymer-coated boards, the water vapor transmission rate (WVTR) is affected by e.g. the coating weight of the polymer as well as the temperature and humidity of the surroundings [3,4]. The common polymers used in packages include low- and high-density polyethylene, polypropylene and polyethylene terephthalate [5]. Hygroscopic materials, such as many biopolymers, typically lose their barrier properties at high relative humidity due to water absorption [6]. There have been some efforts to improve the water vapor and oxygen barrier properties of polymer coatings with e.g. SiO_x layers [7]. Based on our recent studies [8-11] and studies by others [12-14], a thin Al_2O_3 coating layer grown by the atomic layer deposition (ALD) technique could work as a high-quality pore-free barrier film. The ALD technique is a surface-controlled layer-by-layer deposition process based on self-limiting

gas-solid reactions [15]. It is well suited to produce inorganic gas barrier coatings on various materials.

Because of the covalent bonding, the adhesion of ALD-grown Al_2O_3 layer with the substrate is commonly excellent [16,17]. Biopolymers typically have functional surface groups improving the bonding between the substrate and the Al_2O_3 layer. This makes biopolymeric materials, in our opinion, even more interesting substrates to create efficient gas and moisture barrier materials when combined with a thin Al_2O_3 coating than regular oil-based polymers, such as polyethylene, polypropylene or polyethylene terephthalate, for instance.

The ALD film growth characteristics on oil-based polymers have been previously studied by others [18- 21]. Metal oxide films were found to grow on the native substrate surface. The basis for the initial film growth and nucleation was the hydroxyl groups on the polymer [15,22]. The Al_2O_3 growth mechanism on porous polymeric substrates was demonstrated to occur through the adsorption of the trimethylaluminum (TMA) precursor onto the surface or by absorption into the porous material leading to the formation of Al_2O_3 clusters and further on to the linear film growth rate after the nucleation period [19]. The same mechanism has been demonstrated for many polymers. However, the initiation period differs depending on the polymer [18].

Here we demonstrate that ALD is indeed a promising technique to fabricate thin Al_2O_3 barrier layers on bio-based temperature-sensitive packaging materials. We moreover show that the barrier properties can be further improved by coating the materials with a pre-barrier layer prior to the ALD- Al_2O_3 coating.

2. Material and Methods

The packaging materials investigated were commercial boards (provided by Stora Enso Oyj) coated with bio-based polylactide (PLA). In addition, several different biopolymer films were investigated. The materials tested are presented in Table I. From our previous thermogravimetric study performed for most of the present substrate materials [8], we may conclude that the materials do not degrade thermally at temperatures employed in our low-temperature ALD- Al_2O_3 process.

The ALD- Al_2O_3 depositions were carried out at 80 or 100 °C in a Picosun SUNALE™ reactor on substrates that were *ca.* 10 x 10 cm² in size. Trimethylaluminum (TMA, electronic grade purity, SAFC Hitech) and H_2O or O_3 were used as precursors. Ozone was produced by feeding oxygen gas (99.9999%) into the reactor through an ozone generator (In USA Inc., model AC 2025). The concentration of ozone was *ca.* 8% and the gas flow rate during the pulse was about 200 sccm (standard cubic centimeters per minute). High purity nitrogen (99.9999% N_2) was used as a carrier and purge gas. The operating pressure was 1-2 kPa. The precursor pulsing sequence was: 0.1 s TMA pulse, 6 s N_2 purge, 0.1 s H_2O or O_3 pulse, and 6 s N_2 purge, and the number of ALD cycles was adjusted according to the targeted Al_2O_3 coating thickness of 25 nm (selected based on our previous works) [9-11]. The actual thicknesses of the Al_2O_3 films could not be directly measured. Instead, we estimated the thicknesses based on the growth rate determined to be *appr.* 0.1 nm/cycle with a Nanospec AFT4150 reflectometer from films grown on a Si(100) wafer. This

was done for the TMA-H₂O process at both temperatures and for the TMA-O₃ process at 100 °C. Because of the different surface chemistries of different polymers, the actual thickness may somewhat deviate from that determined for the Al₂O₃-coated silicon wafer [20,23]. It should also be mentioned that even though the aim was to deposit only on the polymer-coated side, film growth also on the uncoated side could not be totally prevented.

We also considered the possibility to coat the substrate material with a pre-barrier layer prior to the ALD-Al₂O₃ coating to block the largest pinholes in the porous substrates. For these experiments B2(PLA) substrates were used. Epoxy-based hybrid coatings with targeted coating weight of 2 g/m² were fabricated by a sol-gel (SG) method using 3-(trimethoxysilyl)propyl glycidyl (from Sigma-Aldrich) as an epoxy source, ethanol as a solvent and water to initiate the hydrolysis and condensation reactions. The coatings were sprayed on corona-treated substrates and dried at 120 °C for 10 min. The corona treatment unit (ET1 from Vetaphone) with treatment time of 60 s was used for better wetting and adhesion properties between the coating and the substrate. The SG-coated substrates were further coated with an Al₂O₃ layer at 80 °C using TMA and H₂O as precursors.

The Al₂O₃-coated samples were characterized by scanning electron microscopy (SEM; Hitachi S-3400 N VP-SEM, operating voltage 15 keV) for the microstructure. Prior to the imaging the samples were sputter-coated with Pt. The surface topography was analyzed with atomic force microscopy (AFM: Park Systems XE-100 equipment with cantilever 905-ACTA) using a non-contact “tapping” mode.

Contact angle (CA) and surface energy (SE) measurements (KSV CAM 200 Optical Contact Angle Meter) were carried out for some of the samples in a controlled atmosphere (relative humidity 50%, temperature 23 °C) with three to eight parallel measurements and expressed as degrees (°). The CA value was determined using water as solvent. For the SE measurements, water and di-iodomethane were used as solvents. The CA values of solvents were calculated at the time of 1 s from the moment the drop contacts. The SE values were calculated from the CA data by using the OWRK (ext. Fowkes) theory and expressed as mN/m.

For all the samples, the oxygen and water vapor transmission rate (OTR, WVTR) values were determined. The OTR values expressed as $\text{cm}^3/\text{m}^2/10^5\text{Pa}/\text{day}$ were measured (Systech M8001 and Mocon Oxtran 2/20) from two to three parallel samples using humid gases at 23 °C and in 50% relative humidity. The WVTR values were measured from three to five parallel samples according to the modified gravimetric methods ISO 2528:1995 and SCAN P 22:68 and were expressed as $\text{g}/\text{m}^2/\text{day}$ in conditions of 23 °C and 75% relative humidity.

3. Results and Discussion

Our first task was to optimize the ALD- Al_2O_3 process for temperature-sensitive bio-based substrates. In these preliminary experiments two PLA-coated board samples, B1(PLA) and B2(PLA), were investigated and the deposition parameters considered were the deposition temperature (80 or 100 °C) and the choice of the oxygen source (H_2O or O_3). Interestingly, the growth per cycle (GPC) values for the H_2O and O_3 processes were found to be nearly identical, i.e. 0.1 nm/cycle (as measured for films grown on silicon substrates). This somewhat disagrees with the work by Elliot *et al.* [22] reporting somewhat lower GPC values for the TMA- O_3 process

compared to the TMA-H₂O process. It seems that in our case the O₃ gas might have been somewhat wet; note that the H₂O present may act as a catalyst for the reactions during the TMA-O₃ process, increasing the GPC value.

The results from the OTR and WVTR experiments for the B1(PLA) and B2(PLA) samples with differently grown Al₂O₃ coatings are shown in Table II. Independent of the deposition parameters used, the 25-nm thick ALD-Al₂O₃ coating remarkably improves both the oxygen and water vapor barrier properties of our PLA-coated board samples. Previous studies have shown that the deposition temperature may have some impact on the surface topography and morphology as well on the adhesion of Al₂O₃ coating in the case of polymeric substrates [24]. Higher deposition temperature may increase crystallinity of the polymers and cause brittleness for polymer structures which could then lead to cracking of the polymer layer impairing the barrier properties. Here however, the choice of the deposition temperature (in the range investigated, i.e. 80-100 °C) may not be crucially important. In some cases even lower deposition temperatures might be advantageous. For extremely temperature-sensitive biopolymeric substrates the low deposition temperature could prevent the curling effect due to polymer shrinkage. Moreover, Lahtinen *et al.* [24], demonstrated that by using lower deposition temperatures it was possible to achieve better adhesion between the polymer surface and the Al₂O₃ coating.

Also, both the processes, TMA-H₂O and TMA-O₃, apparently work well at least for the PLA-coated boards. This could be due to the different fabrication methods of the pristine substrates. From Table II, the OTR values achieved are somewhat better in the case of the TMA-O₃ process, while the opposite seems to be true for the WVTR values. During the water pulse, the absorbed

H₂O may cause the polymer to swell, which should not be the case with O₃. OTR is generally regarded as more sensitive towards coating defects than WVTR. Hence, the TMA-O₃ process can be considered a highly potential alternative for depositing Al₂O₃ coatings on biopolymers except for the most sensitive materials not standing the strong oxidation power of O₃.

We should also consider the moisture within the polymer chains of the substrate material. Bio-based substrates tend to contain absorbed moisture and the removal of it could enhance the barrier properties because absorbed water may act as a plasticizer impairing the barrier properties. The possible benefits of the removal of the substrate moisture prior to the ALD-Al₂O₃ deposition were investigated by keeping a B1(PLA) sample in a heated (100 °C) ALD reactor chamber overnight before coating it with Al₂O₃ at 100 °C using the TMA-H₂O process. The overnight heat-treatment resulted in a slight improvement in the OTR value: the value decreased from 20 to 8 cm³/m²/10⁵Pa/day. However, the effect on the WVTR value was just the opposite: it increased from 1 to 7 g/m²/day. The removal of the moisture within the polymer chains made the sample brittle.

The main scope of the present work was to investigate whether the excellent results obtained for the PLA-coated boards with ALD-grown Al₂O₃ coatings could be extended to other bio-based materials. The oxygen and water vapor barrier results achieved for a variety of biopolymer substrates with a 25 nm-thick Al₂O₃ layer deposited by the TMA-H₂O process are summarized in Figure 1. Note that H₂O was used as the oxygen source instead of O₃ to be sure that the results would not be distorted by the possible harmful effects of O₃ in the case of the most sensitive biopolymer film substrates. The depositions were performed at 80 or 100 °C depending on the

expected temperature tolerance of the substrate material. From Figure 1, it can be concluded that our ALD-Al₂O₃-coated PLA, pectin, NFC, B1(PLA) and B(GGM) samples are highly promising oxygen barriers with OTR values that are already close to the oxygen barrier level required for dry food applications. For example, for PLA1 and B1(PLA) the OTR values were improved from 702 to 43 cm³/m²/10⁵Pa/day and from 420 to 20 cm³/m²/10⁵Pa/day, respectively. Besides being a good oxygen barrier, the Al₂O₃-coated B1(PLA) sample is also a highly promising water vapor barrier as the WVTR value of it was improved from 65 to 1 g/m²/day.

The NFC film investigated here is a highly interesting fiber network for various potential applications. Besides enhancing the oxygen barrier of NFC, the ALD-Al₂O₃ coating works as a kind of protective layer for the nanofibers (Figure 2). Such materials are in the very focus of current research interest as examples of the controlled material integration of organic fibers and inorganic thin films [25]. This type of uniform coatings on single fibers are believed to open up new application possibilities e.g. in the area of filter development.

Despite the promising results achieved so far for the ALD-Al₂O₃ coated bio-based materials here and in our earlier studies [8-11], further improvements are still desired. A pre-barrier layer could close the larger pinholes on the surface of porous substrate making it denser and probably smoother and thus more favorable surface for the Al₂O₃ barrier layers to be grown on. The effect of a sol-gel coating between the substrate and the top ALD-Al₂O₃ coating was studied using B2(PLA) as a substrate material. In Figure 3, AFM surface and phase images for plain, SG-coated and SG+Al₂O₃-coated B2(PLA) are presented. The observed average roughness (R_a) values are also given. From Figure 3, the SG coating decreases the R_a value making the surface

of the substrate smoother. The ALD- Al_2O_3 layer on top of the SG coating makes the surface even smoother. The total decrease in R_a was from 54 to 15 nm.

We also determined the contact angle (CA) and surface energy (SE) values for plain, SG-coated and SG-+ Al_2O_3 -coated B2(PLA), see Table III. The SG coating decreases the CA value indicating a more hydrophilic surface. The CA value drops even further with the additional Al_2O_3 coating. In Table 3, also given are the OTR and WVTR values for the same samples. The results show a moderate positive effect of SG coating on the barrier properties of B2(PLA). Only after the SG-coated B2(PLA) was additionally coated with Al_2O_3 , the appreciably low OTR and WVTR values of $2 \text{ cm}^3/\text{m}^2/10^5 \text{ Pa/day}$ and $2 \text{ g}/\text{m}^2/\text{day}$, respectively, were reached. Most importantly, these values are lower than those achieved for B2(PLA) with the ALD- Al_2O_3 coating only, i.e. $6 \text{ cm}^3/\text{m}^2/10^5 \text{ Pa/day}$ and $3 \text{ g}/\text{m}^2/\text{day}$, respectively.

4. Conclusions

We have demonstrated that the oxygen and water vapor barrier properties of various bio-based boards and films are significantly enhanced by coating them with a 25-nm thick ALD-grown Al_2O_3 film. Through careful process optimization excellent barrier properties were reached for some of the bio-based materials investigated such that the materials satisfy the basic requirements set for commercial barrier materials for dry food or pharmaceutical packaging applications. Also shown was that there are means to improve the barrier properties further by cheap and easy-to-make coatings applied on the substrate surface prior to the top ALD- Al_2O_3 coating. In the future

these materials could be produced with a continuous ALD process. There are already research tools and several patent applications concerning the development of the continuous ALD process.

Acknowledgements

The authors thank VTT and Academy of Finland (No: 126528) for funding. Stora Enso Oyj and polymer film suppliers are thanked for providing the substrates. The facilities of Nanomicroscopy Center, Aalto University were also used during this research.

References

- [1] K. Khwaldia, E. Arab-Tehrany, S. Desobry, *CRFSFS* 1 (2010) 82-91.
- [2] C. Andersson, *Packag. Technol. Sci.* 2 (2008) 339-372.
- [3] J. Kuusipalo, K. Lahtinen, *TAPPI J.* 7 (2008) 8-15.
- [4] A. Savolainen, J. Kuusipalo, E. Laiho, T. Penttinen, in: A. Savolainen (Eds.), *Paper and Paperboard Converting*, Fapet Oy, Helsinki Finland, 1998, pp.123–187.
- [5] J. Lange, Y. Wyser, *Packag. Technol. Sci.* 16 (2003) 149-158.
- [6] Y. Leterrier, *Prog. Mater. Sci.* 48 (2003) 1-55.
- [7] A. Sorrentino, M. Tortora, V. J. Vittoria, *Polymer Sci. B* 44 (2006) 265-274.
- [8] T. Hirvikorpi, M. Vähä-Nissi, T. Mustonen, E. Iiskola, M. Karppinen, *Thin Solid Films* 518 (2010) 2654-2658.
- [9] T. Hirvikorpi, M. Vähä-Nissi, A. Harlin, M. Karppinen, *Thin Solid Films* 518 (2010) 5463-5466.
- [10] T. Hirvikorpi, M. Vähä-Nissi, A. Harlin, J. Marles, V. Miikkulainen, M. Karppinen, *Appl. Surf. Sci.* 257 (2010) 736-740.
- [11] T. Hirvikorpi, M. Vähä-Nissi, J. Vartiainen, P. Penttilä, J. Nikkola, A. Harlin, R. Serimaa, M. Karppinen, *J. Appl. Polymer Sci.* (2011) in press.
- [12] M. D. Groner, S. M. George, R. S. McLean, P. F. Carcia, *Appl. Phys. Lett.* 88 (2006) 051907-1-3.
- [13] P. F. Carcia, R. S. McLean, M. H. Reilly, M. D. Groner, S. M. George, *S.M. Appl. Phys. Lett.* 89 (2006) 031915-1-3.

- [14] S.H.K. Park, J. Oh, C. S. Hwang, J. I. Lee, Y. S. Yang, H. Y. Chu, H.Y. Electrochem. Solid-State Lett. 8 (2005) H21-H23.
- [15] R. L. Puurunen, J. Appl. Phys. 97 (2005) 121301-1-52.
- [16] T.O. Kääriäinen, D.C. Cameron, M. Tantari, Plasma Process. Polym. 6 (2009) 631-641.
- [17] D.C. Miller, R.R. Foster, Y. Zhang, S.-H. Jen, J.A. Bertrand, Z. Lu, D. Seghete, J.L. O'Patchen, R. Yang, Y.-C. Lee, S.M. George, M.L. Dunn, J. Appl. Phys. 105 (2009) 093527-12.
- [18] M. D. Groner, F. H. Fabreguette, J. W. Elam, S. M. George, Chem. Mater. 16 (2004) 639-645.
- [19] C. A. Wilson, R. K. Grubbs, S. M. George, Chem. Mater. 17 (2005) 5625-5634.
- [20] J. D. Ferguson, A. W. Weimer, S. M. George, Chem. Mater. 16 (2004), 5602-5609.
- [21] C. A. Wilson, J. A. McCormick, A. S. Cavanagh, D. N. Goldstein, A. W. Weimer, S.M. George, Thin Solid Films 516 (2008) 6175-6185.
- [22] S. D. Elliot, G. Scarel, C. Wiemer, M. Fanciulli, G. Pavia, Chem. Mater. 18 (2006) 3764-3773.
- [23] X. H. Liang, L. F. Hakim, G. D. Zhan, J. A. McCormick, S. M. George, A. W. Weimer, J. A. Spencer, K. J. Buechler, J. Blackson, C. J. Wood, J. R. Dorgan, J. Am. Ceram. Soc. 90 (2007) 57-63.
- [24] K. Lahtinen, P. Maydannik, P. Johansson, T.Kääriäinen, D. C. Cameron, J. Kuusipalo, Surf. Coat. Technol. 205 (2011) 3916-3922.
- [25] J. S. Jur, J. C. Spagnola, K. Lee, B. Gong, Q. Peng, G. N. Parsons, Langmuir 26 (2010) 8239-8244.

Table I. Packaging materials employed as substrates.

Code	Description
B1(PLA)	Poly lactide-coated board; PLA 35 g/m ² , board 310 g/m ²
B2(PLA)	Poly lactide-coated board; PLA 35 g/m ² , board 210 g/m ²
B3(PLA)	Poly lactide-coated board; PLA 27 g/m ² , board 210 g/m ²
PLA1	Poly lactide film, 20 μm
PLA2	Poly lactide film, 75 μm
NFC	Nano-fibrillated cellulose film; NFC; appr. 60 g/m ²
B(GGM)	Galactoclugomannan-coated board; GGM appr. 9 g/m ² , board 200 g/m ² pigment coated
PHB	Polyhydroxy butyrate film, 180 μm
Pectin	Pectin film made by solution casting, 160 μm

Table II. OTR and WVTR values for plain and variously ALD-Al₂O₃-coated B1(PLA) and B2(PLA) samples. The ALD parameters investigated were the deposition temperature (80 or 100 °C) and the choice of the oxygen source (H₂O or O₃).

Sample	OTR (cm ³ /m ² /10 ⁵ Pa/day)	WVTR (g/m ² /day)
B1(PLA) uncoated	420 ± 10	65 ± 2
B1(PLA) + Al ₂ O ₃ by H ₂ O (100 °C)	20 ± 3	1 ± 0.2
B1(PLA) + Al ₂ O ₃ by O ₃ (100 °C)	12 ± 1	5 ± 2
B2(PLA) uncoated	400 ± 9	75 ± 2
B2(PLA) + Al ₂ O ₃ by H ₂ O (80 °C)	6 ± 1	3 ± 1
B2(PLA) + Al ₂ O ₃ by O ₃ (80 °C)	3 ± 1	7 ± 2
B2(PLA) + Al ₂ O ₃ by O ₃ (100 °C)	2 ± 0.2	1 ± 0.2

Table III. Contact angle (CA), surface energy (SE), OTR and WVTR values for plain, SG-, SG+Al₂O₃-, and Al₂O₃-coated B2(PLA). The total value of surface energy (SE) is the sum of dispersive (SE_d) and polar (SE_p) components.

Sample	CA (°)	SE _p (mN/m)	SE _d (mN/m)	SE (mN/m)	OTR (cm ³ /m ² /10 ⁵ Pa/day)	WVTR (g/m ² /day)
B2(PLA) uncoated	71	7.4	38.2	45.6	400 ± 9	75 ± 2
B2(PLA) + SG	58	13.2	40.6	53.8	310 ± 2	44 ± 2
B2(PLA) + SG + Al ₂ O ₃	52	18.0	36.9	54.9	2 ± 1	2 ± 1
B2(PLA) + Al ₂ O ₃	-	-	-	-	6 ± 1	3 ± 1

Figure captions:

Figure 1. Oxygen and water vapor barrier results achieved for various bio-based substrate materials (open markers) by means of a 25-nm thick ALD- Al_2O_3 coating (filled markers). The depositions were carried out at 80 or 100 °C using the TMA- H_2O process.

Figure 2. SEM image (*left image*) with a magnification (*right image*) of NFC coated with a 25-nm thick Al_2O_3 layer, showing that the nano-fibrillated fibers are indeed uniformly coated with Al_2O_3 . The smallest observed fiber thickness is *ca.* 50 nm and the curve radius from the fiber ends is appr. 25 nm.

Figure 3. AFM surface topography (*left image*) and phase (*right image*) images of plain, SG- and SG + Al_2O_3 -coated B2(PLA).

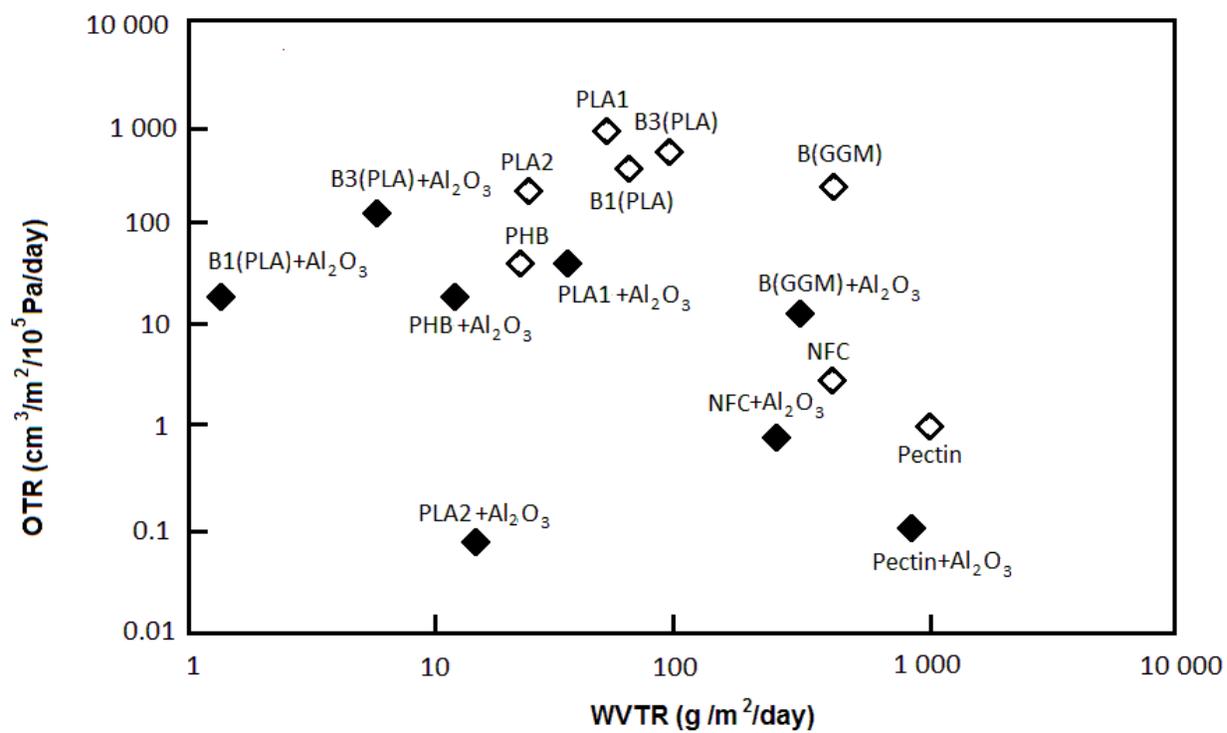


Figure 1.

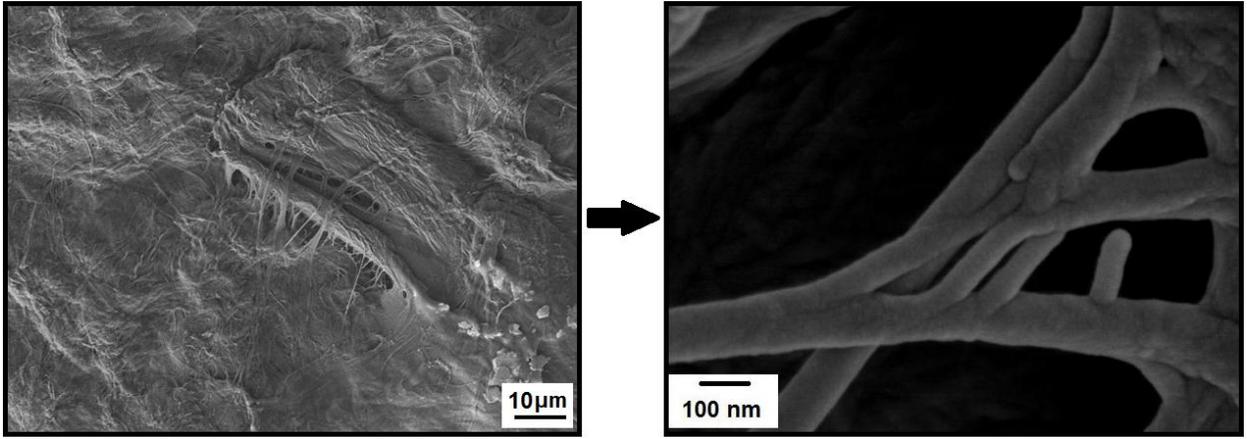


Figure 2.

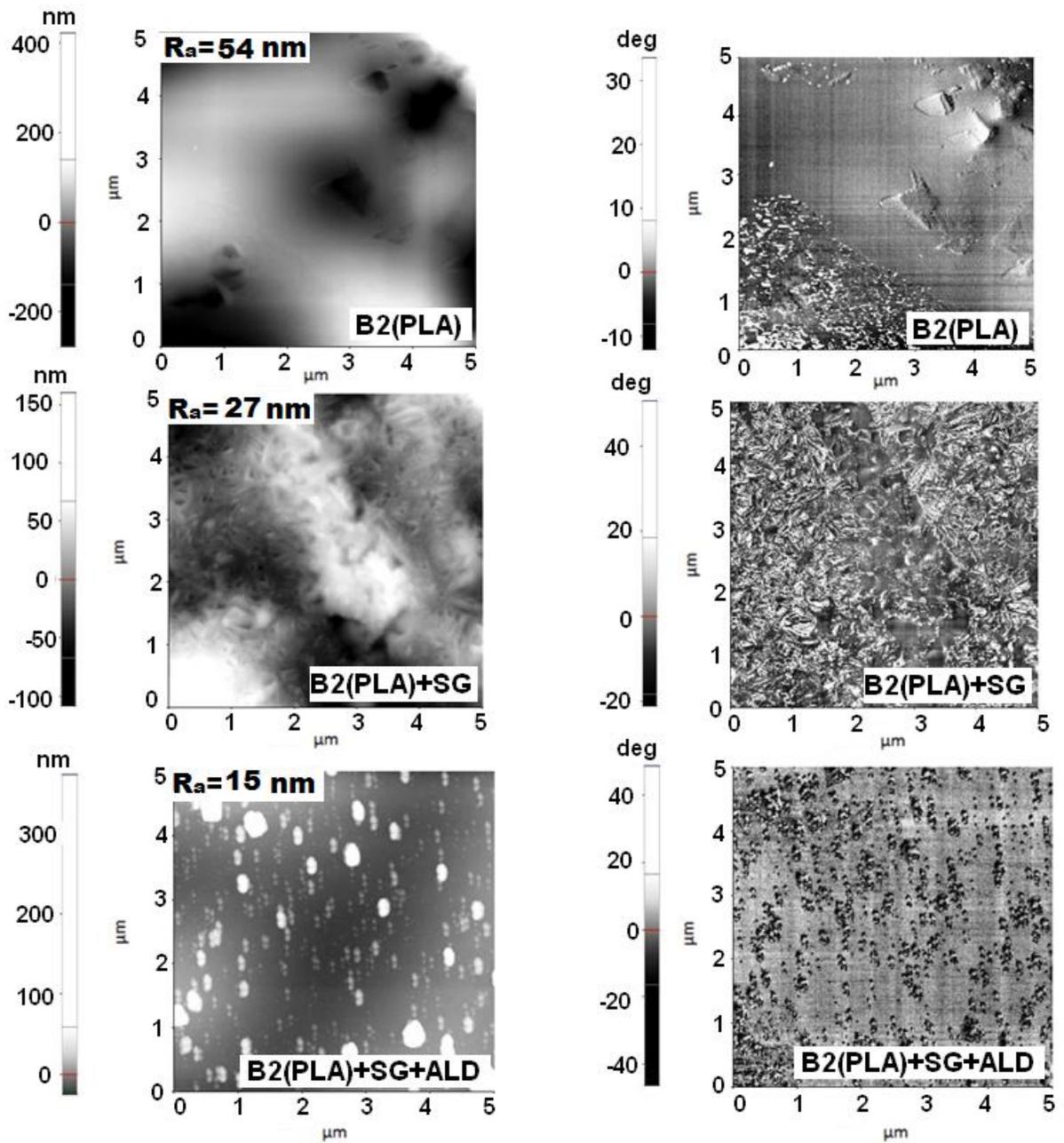


Figure 3.