

Low-temperature, ultra-giant blistering of atomic layer deposited barrier coatings on polyethylene films caused by additive segregation

János J. Tomán^{a,*}, Eszter Baradács^a, Gergő Vecsei^{a,b}, Lajos Nagy^c, Bence Parditka^a, Sándor Kéki^c, Zoltán Erdélyi^a

^a Department of Solid State Physics, Faculty of Science and Technology, University of Debrecen, P.O. Box 400, H-4002 Debrecen, Hungary

^b University of Debrecen, Doctoral School of Physics, Debrecen, Hungary

^c Department of Applied Chemistry, Faculty of Science and Technology, University of Debrecen, Egyetem tér 1., H-4032 Debrecen, Hungary

ARTICLE INFO

Keywords:

Polyethylene
Atomic layer deposition
Flexible coating
Blistering
Cracking
Barrier
Segregation

ABSTRACT

Low-temperature plasma enhanced atomic layer deposition (PE-ALD) is an advanced method for coating flexible polyolefin polymers such as low-density polyethylene (LDPE) to improve their barrier properties against moisture and gases. The ALD process is highly sensitive to surface preparation, and LDPE is challenging to coat due to its highly non-polar nature. In this work, we reveal how the segregation of polymer additives to the surface (commonly known as blooming) can compromise the effectiveness of the barrier coatings. After coating a 10 µm thick LDPE film with a 50 nm thick Al₂O₃ layer using low-temperature PE-ALD, we observed the formation of ultra-giant blisters (larger than previously reported) within minutes of removing the sample from the processing chamber. Our conclusion is that the segregated antioxidant component, tris(2,4-di-tert-butylphenyl)phosphite, traps some of the trimethylaluminium (TMA) used as an ALD precursor. After deposition, the trapped TMA reacts with the moisture in the environment and the gaseous reaction product leads to the formation of ultra-giant blisters with bubble diameters ranging from hundreds of microns to over a millimeter. The bursting of these bubbles creates discontinuities and an increased number of cracks in the 50 nm thick alumina coating, hugely deteriorating its barrier properties. This is a previously unknown failure mode of ALD layers deposited on polymer films as interactions with additives are rarely investigated. We also demonstrate how the appropriate pre-treatments can effectively mitigate this problem, improving the coating's reliability.

1. Introduction

Flexible polymeric materials are of great importance in many industrial applications, from food packaging to numerous electronic applications. In electronics, these materials are frequently used for flexible displays and for fabricating batteries, circuits, semiconductor logic, and memory devices [1]. They are also applied in biomedical fields for sensors, wound dressings and implants [2]. However, the surfaces of these materials are often modified by depositing thin films on them to improve barrier properties and control surface adhesion [1,2]. Atomic layer deposition (ALD) is one of the most relevant coating techniques, as it is suitable for the synthesis of high-quality, nanoscale films at the sub-monolayer level at low temperatures. Moreover, the surface of polyolefins, like that of low-density polyethylene (LDPE), is highly non-polar, which leads to poor printability, bonding, and coating properties, which must be overcome in several utilizations, such as ALD [3].

Plasma-enhanced ALD (PE-ALD) shows several advantages for the deposition of nanofilms, such as the low process temperature, the ability to use a wide range of precursors, and high film quality and uniformity [4].

ALD layers are highly sensitive to the quality and chemical state of the surface which they are deposited on [5–7]. One of the many problems that can arise from interactions between the ALD layer and its substrate is blistering, that is, the formation of bubbles between the substrate and the deposited layer. Blistering in thin films deposited by ALD is a well-known and reasonably well-understood phenomenon on certain substrate materials [6–8]. It usually occurs during the post-deposition heat-treatment of the device, which is unavoidable in most applications of ALD layers. For example, in solar cell manufacturing, ALD Al₂O₃ layer can be used for back-side passivation of solar cells, and that is a very early step in the solar cell manufacturing process [9]. During several high-temperature processing steps following the atomic

* Corresponding author.

E-mail address: janos.toman@science.unideb.hu (J.J. Tomán).

<https://doi.org/10.1016/j.porgcoat.2025.109261>

Received 28 September 2024; Received in revised form 7 March 2025; Accepted 19 March 2025

Available online 28 March 2025

0300-9440/© 2025 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

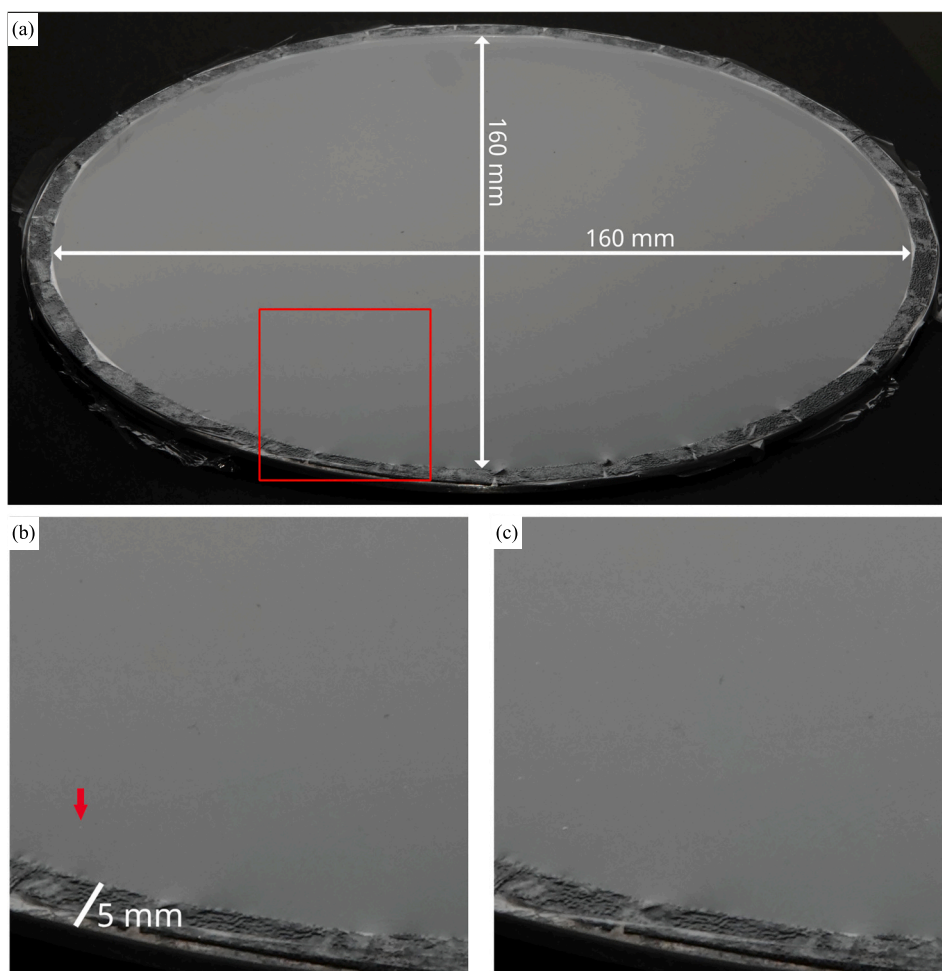


Fig. 1. A series of photographs of the same sample region over 12 min, (a) photograph of the whole sample with the dimensions shown to demonstrate how the low viewing angle of the camera distorts the distances in the image; a frame shows the magnified region in the other subfigures, (b) showing the first bubble marked by a red arrow (the scale bar is just a guidance due to the geometric distortion) (c) after 70 s (d) after 106 s (e) after 198 s (f) after 458 s (g) after 725 s.

layer deposition, blistering can occur, causing a decrease in the performance of the device [10]. There is strong evidence that this blistering is caused by the hydrogen released from the alumina layer deposited by ALD and accumulated at the Al_2O_3 /substrate interface forming macroscopic-sized bubbles [8]. Since this type of blistering occurs only during high-temperature annealing (several hundred degrees), one might assume that low-temperature applications, such as coatings of polyolefins, are unaffected. However, the main reason behind blistering is exactly the same as why we often use ALD deposited Al_2O_3 layers, their excellent gas barrier properties. In the case of solar cell backside surface passivation, the use of a thinner alumina layer will strongly decrease the level of blistering while only somewhat decreasing the effectiveness of the passivation [10].

As we will show in this work, blistering can also be caused by gases coming from the substrate. In the case discussed here, the cause of bubble formation is the segregation of an additive to the surface of the polymer substrate and its interaction with the ALD process and the environment. This results in blistering of the ALD layer at room temperature, which is a newly described phenomenon. Furthermore, while the interactions between the ALD precursor and polymer materials have been investigated before, the research on the interaction of the precursor with the polymer additives is severely lacking. We would like to point out the importance of this field of research because additives can be a very significant proportion of a polymer by mass.

2. Experimental

2.1. Materials and sample preparation

Commercial 10 μm thick LDPE films, often used for food packaging applications, were used as the substrate for the experiments. LDPE sheets were meticulously cut and affixed onto a purpose-made 16 cm diameter ring specimen holder. The edges were adhered using a double-sided carbon tape, a material commonly utilized in electron microscopy, ensuring a secure hold. Subsequently, the sheets were placed within the pre-heated reaction chamber of the Beneq® TFS-200-186 ALD (Beneq Oy, Vantaa, Finland). Plasma-enhanced atomic layer depositions were carried out using a capacitively coupled radio frequency plasma unit (13.56 MHz) with showerhead type electrode assembly. The plasma gas had a composition of 50 % O_2 (99.999 %, Linde®) and 50 % N_2 (99.996 %, Linde®) and the radio frequency power was 50 W. The reactor temperature was 38 °C, the reactor pressure was maintained around 1.4 mbar. A 50 nm thick Al_2O_3 layer was deposited on the LDPE sheets using trimethylaluminium (TMA, 97 %, Sigma-Aldrich®) and remote N_2/O_2 plasma as precursors. An ALD cycle is comprised of two half-cycles. The first half-cycle consists of a TMA pulse and purge, whilst the second half-cycle consists of N_2/O_2 plasma pulse and purge. The pulse times were 150 ms for the TMA and 2000 ms for the N_2/O_2 plasma. Both were followed by a 2 s nitrogen purge for 224 ALD cycles in total. Samples were prepared in two ways: i) deposition on as-received LDPE, and ii)

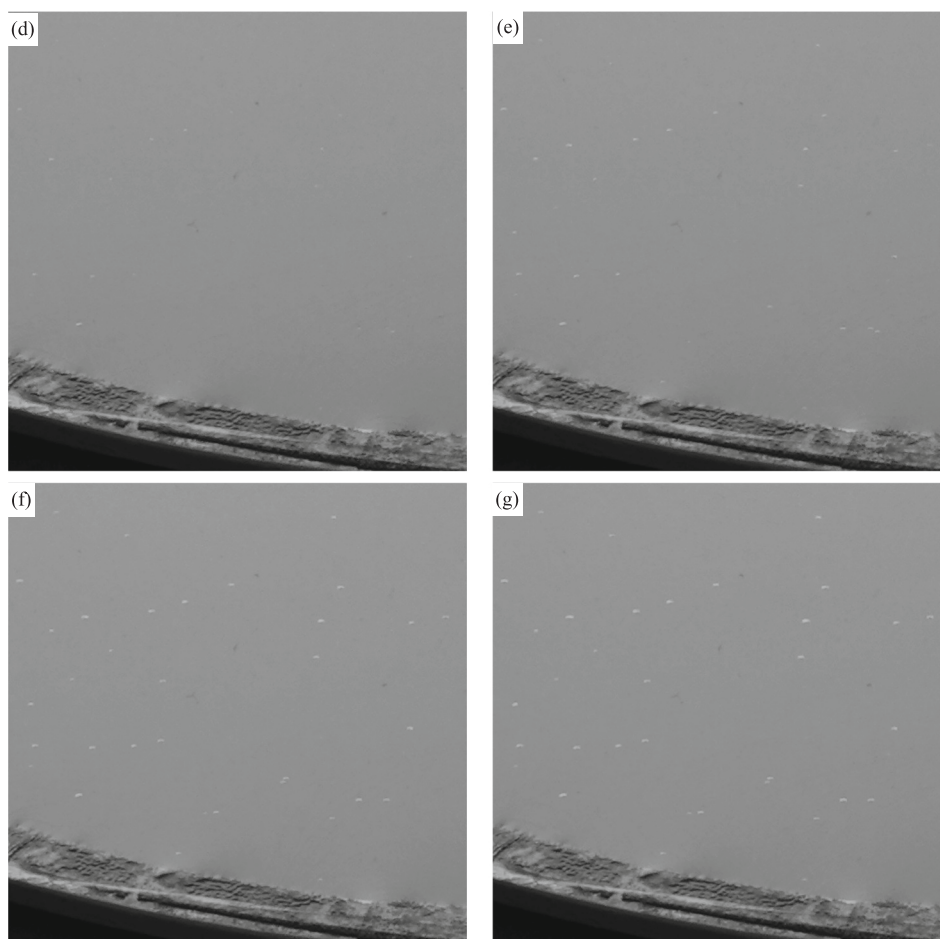


Fig. 1. (continued).

LDPE was plasma treated in the ALD reactor before deposition.

2.2. Sample imaging

The post-deposition formation of the blisters was investigated in-situ by a SONY digital camera and special lighting conditions to reveal the microscopic details of the sample. To analyze the samples ex-situ, we used a ZEISS Axio Scope A1 microscope in bright field (BF) and circular differential interference contrast (C-DIC) mode using reflected-light beam path.

2.3. Electrospray ionization mass spectrometry (ESI-MS)

ESI-MS measurements were performed with a MicroTOF-Q type Qq-TOF MS instrument equipped with an electrospray ion source from Bruker (Bruker Daltonik, Bremen, Germany). Nebulizing gases (0.4 bar) and drying gases (4 L/min) were nitrogen and the drying gas temperature was kept at 200 °C. The needle voltage was 4 kV. The isopropanol solution eluted from the ALD-LDPE surface was directly introduced into the ion source using a syringe pump at a flow rate of 3 μ L/min. The mass spectra were calibrated externally using the exact masses of the clusters generated from the electrosprayed solution of sodium trifluoroacetate (NaTFA).

3. Results and discussion

3.1. Blister formation at room temperature

Blister formation was observed in the samples after the plasma

enhanced atomic layer deposition was completed, and the samples were removed from the reaction chamber. Notably, blister formation occurs only outside of the reaction chamber. This was also confirmed by the fact that we kept some of the as-prepared samples in the reaction chamber's low-pressure nitrogen environment for several hours, and blistering started only after the samples were removed from the reactor. The growth of these bubbles began a few minutes after the sample was removed from the reaction chamber and the growth process took place within a few minutes. For demonstration purposes, we show a series of photographs in Fig. 1, taken over 12 min after the appearance of the first bubble. Subsequent images did not show a noticeable difference. These observations indicate that bubble formation begins upon exposure of the samples to ambient air (oxygen or humidity), leading to gas formation at the LDPE/ Al_2O_3 interface.

Blistering of an ALD layer at room temperature is rather puzzling, and we did not find any references to it in the scientific literature. As we mentioned earlier, blistering usually occurs during high-temperature heat-treatments after deposition.

3.2. Bursting blisters and crack formation

The alumina layers are expected to exhibit limited elasticity, even with a thickness of 50 nm. The formation of cracks in the coating is expected and its effect on the barrier properties of the layer is anticipated. If we change the lighting conditions for photographing the surface of the sample and introduce a light intensity gradient, we can reveal one of the most important problems that is caused by blistering. Some of the forming bubbles burst, and this violent release of stress creates an increased number of cracks in the layer that will significantly impact its

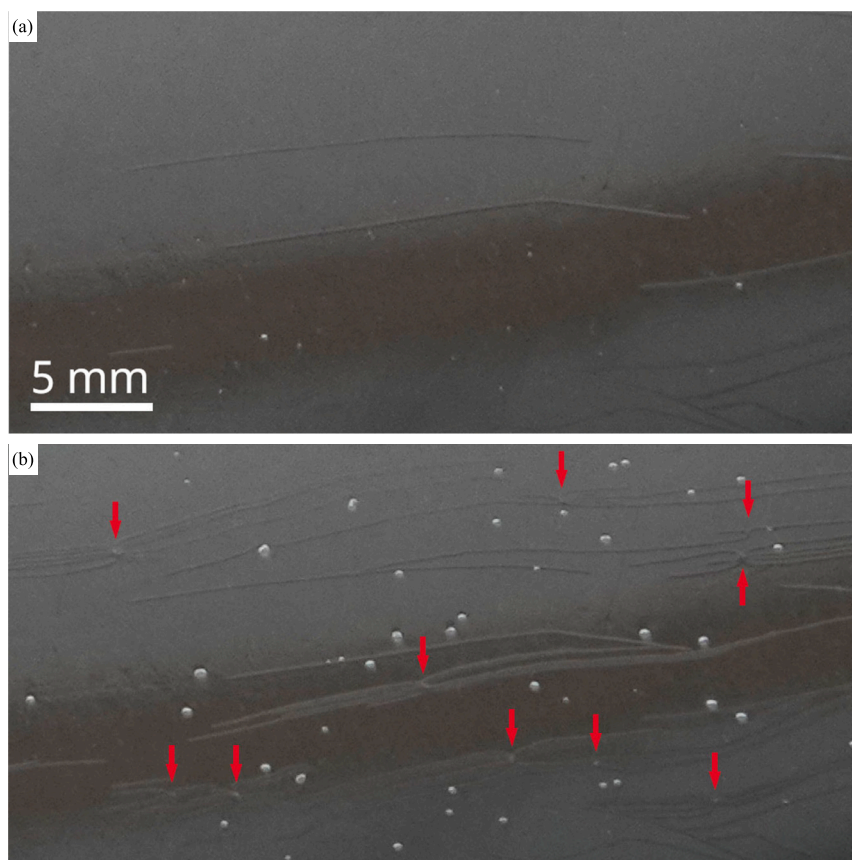


Fig. 2. The bursting bubbles increased the number of cracks in the alumina layer. (a) Early stage of bubble formation. The scale bar is just a guidance, as the low viewing angle of the camera distorts the distances in the image (see Fig. 1(a)). (b) Later stage of bubble formation (2 min after (a) subfigure) with burst bubbles indicated by red arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

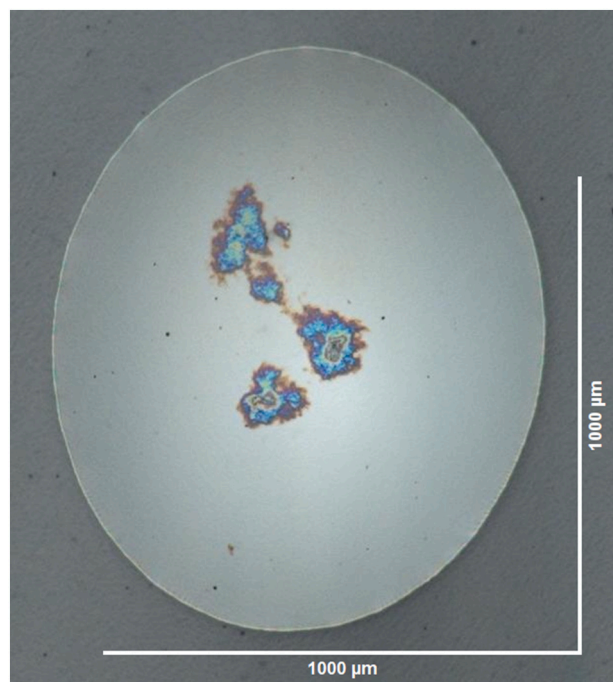


Fig. 3. Bright field optical microscope image of one of the largest bubbles.

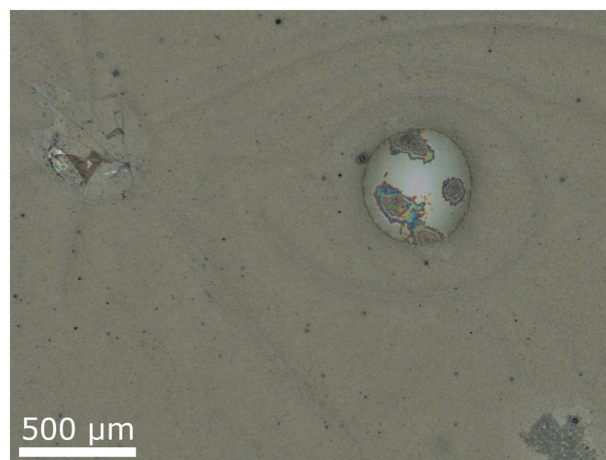


Fig. 4. Bright field optical microscope image of the interaction between the cracks formed by a bursting bubble and another bubble.

performance as a barrier [11]. In Fig. 2, we show the cracks caused by bubbles that burst during growth. Furthermore, at the location of the burst blisters, serious discontinuities form in the layer, which can have an even larger impact on the barrier performance than the cumulative effect of the cracks.

3.3. Ultra-giant blisters

To understand the cause of the blister formation, at first, we turned

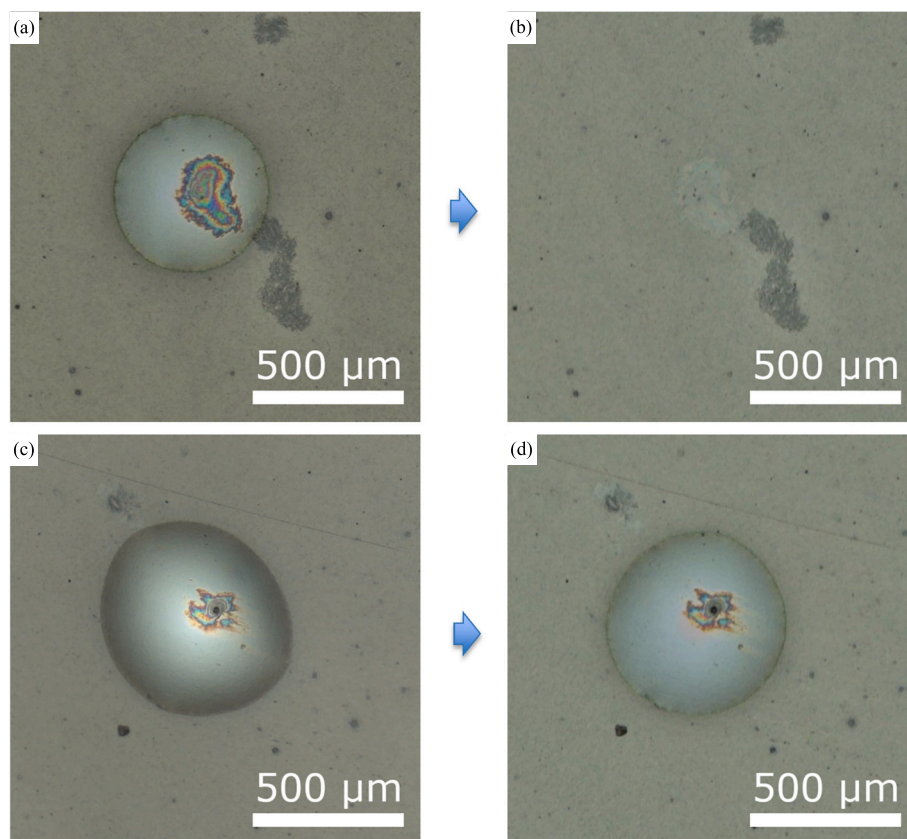


Fig. 5. Two different fates of bubbles on a sample that has been stored at room temperature for one week in 50 % average relative humidity. In subfigures (a) and (b), we demonstrate the most common fate, where the bubble simply flattens as the trapped gas diffuses out. In subfigures (c) and (d), we show a rare bubble that survived the one-week treatment, although it is clear that it took on a more rounded shape to release some of the stress that raised during its formation. (Dark stamps in the figures are the segregated component, but on the other side of the LDPE film.)

to optical microscopy. The bubbles measure hundreds of microns or even exceeding one millimeter in diameter. (See an example in Fig. 3.) This is especially noteworthy as these blisters are even exceeding the size of previously reported “giant blisters” that have been achieved by annealing an ALD $\text{Al}_2\text{O}_3/\text{ZnO}$ film stack on sapphire at elevated temperatures [12].

3.4. Complex stress fields in the alumina layer

The formation of cracks in the alumina layer when a bubble bursts was already an indication that the stresses emerging in the alumina barrier coating are quite significant. It is known that large stresses are emerging in an ALD Al_2O_3 layer deposited on a polymer and the elastic mismatch enhances cracking [13]. In Fig. 4, we show an interesting case where the cracks that formed during the burst of a bubble interact with the stress field that is caused by the growth of another bubble. Note how the cracks can completely curve around the blistered area. We can also see, that the bursting bubble causes severe discontinuity in the alumina layer.

3.5. Long-term change of blisters

Keeping a sample at room temperature in ambient air for one week reveals that the alumina layer is surprisingly elastic (see Fig. 5 (a)-(b)), as in most cases, the bubbles simply flattened as the trapped gas diffused out through the polymer film or by diffusing along the Al_2O_3 /LDPE interface, escaped through nearby cracks. However, some bubbles survived the one-week treatment, although they took on a more rounded shape to release some of the stress that developed during their formation (see Fig. 5 (c)-(d)).

3.6. The possible role of the segregated component

Under the microscope, it could be observed that there are some inhomogeneities (patches) on the surface of the as-received LDPE films. Furthermore, colored areas can be seen in all of the microscope images of the bubbles, suggesting that the appearance of the bubbles is related to the material on the surface (see, e.g. Figs. 3–5). On the basis of the microscopic images, we suspected that the patches could be a segregated (bloomed) component of the LDPE film instead of a surface contamination. Several additives can segregate to the surface of polymers as they form a non-compatible (phase-separating) mixture with the matrix. Sometimes this behavior is beneficial as it is in cling films, where a tackifier component (e.g. polyisobutylene) segregating to the surface improves the film’s adhesion properties [14]. In other cases, segregation is unfavorable. Antioxidants are especially affected by this phenomenon. During production and storage these components can migrate to the surface decreasing the clarity of transparent products (blooming) [15]. Segregation can also cause problems in the production equipment as the segregated antioxidants can build-up e.g. on the rollers (plate-out) [16,17].

3.7. Effect of plasma pre-treatment on the segregated component and blistering

It is a common practice to apply direct or indirect plasma pre-treatments on polymer films before adding any surface coating to increase the adhesion between the two layers [18–20]. Plasma treatments achieve this by increasing the number of certain active functional groups, like hydroxy ($\text{C}-\text{OH}$) and carbonyl ($\text{C}=\text{O}$) groups [18,21].

When using the same gas mixture as during deposition, we applied a

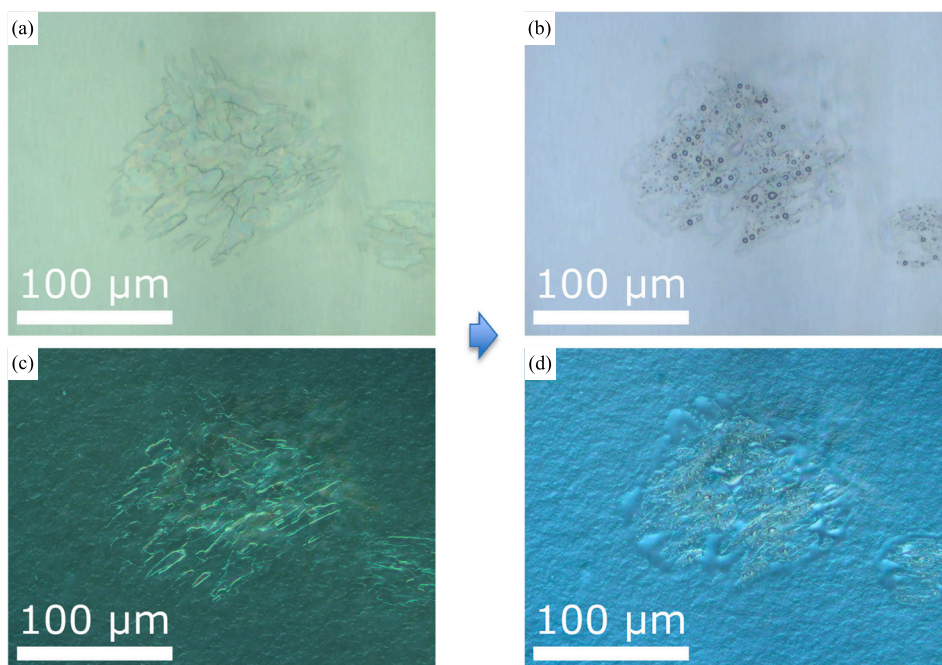


Fig. 6. The reaction of the segregated component to 10 s plasma treatment on the treated front side as seen in an optical microscope. (a) BF image before plasma treatment, (b) BF image after plasma treatment, (c) C-DIC image before plasma treatment, (d) C-DIC image after plasma treatment.

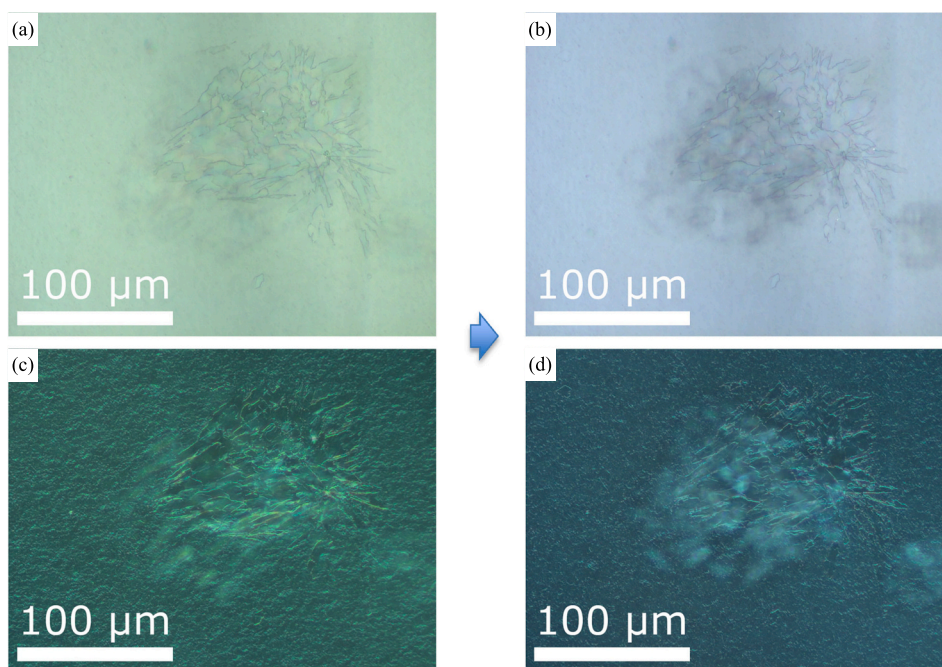


Fig. 7. The reaction of the segregated component to 10 s plasma treatment on the untreated back side at the same place as Fig. 6. (a) BF image before plasma treatment, (b) BF image after plasma treatment, (c) C-DIC image before plasma treatment, (d) C-DIC image after plasma treatment.

10 s plasma pre-treatment before the PE-ALD deposition, we did not observe bubble formation. Therefore, plasma pretreatment must clearly have an effect on the patches. Figs. 6(a) and 6(c) show what the patches look like on the as-received surface using both the bright-field (BF) and circular differential interference contrast (C-DIC) mode of the optical microscope, while in Figs. 6(b) and 6(d) we can see the impact of plasma treatment on them. To demonstrate that this is indeed the result of the plasma treatment and not just the increased temperature of the reactor, we focused the optical microscope on the other, untreated side of the

polymer film, too, (taking advantage of the transparency of the LDPE film) revealing that the patches are practically unchanged on the untreated side (see Fig. 7). Note that Figs. 6 and 7 show the exact same region just focused at the front or at the back of the LDPE film.

3.8. Identifying the bloomed component by mass spectrometry

To investigate the nature of the segregated component, we washed the sample under flowing isopropanol, without any additional

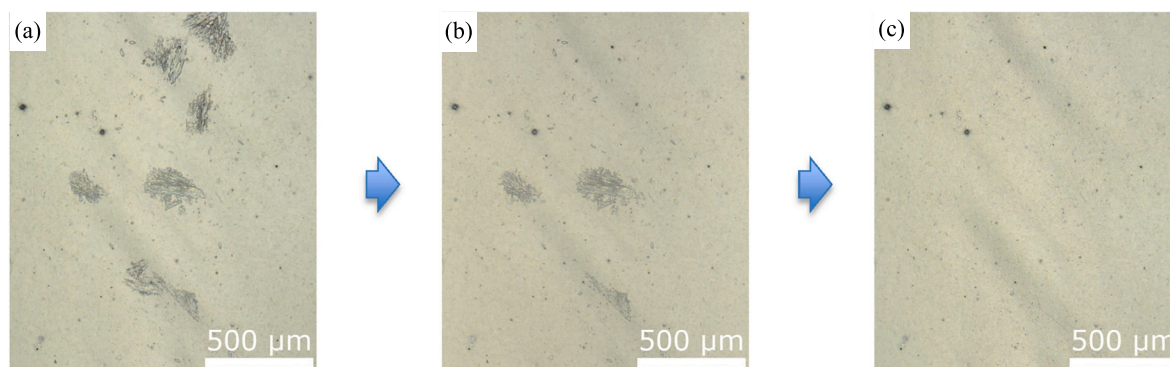


Fig. 8. Washing the sample under flowing isopropanol (without any additional mechanical disturbance) cleans the surface of the bloomed component. (a) An area with bloomed component. (b) The same area after washing one side with isopropanol. (c) The same area after washing both sides with isopropanol.

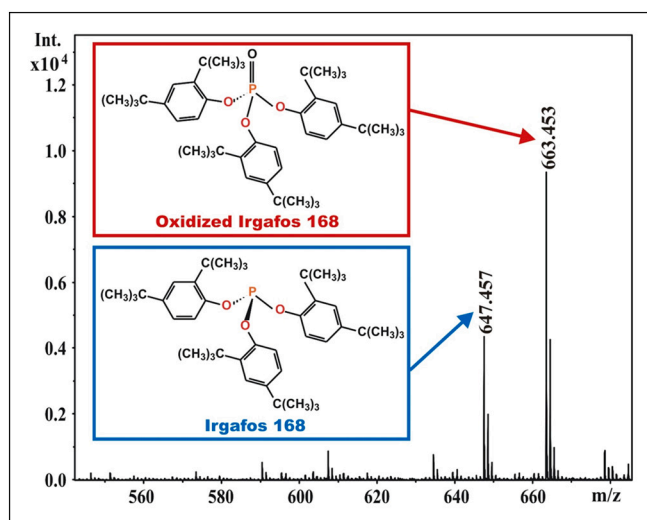


Fig. 9. ESI-MS spectrum of the eluted isopropanol, revealing the segregated component.

mechanical disturbance, which cleaned the surface from the patches (see Fig. 8). This suggests that the segregated component is soluble in isopropanol. Performing the ALD deposition (without plasma pretreatment) on this cleaned sample, resulted in no bubble formation, confirming our theory about the relationship of the material on the surface and the blisters.

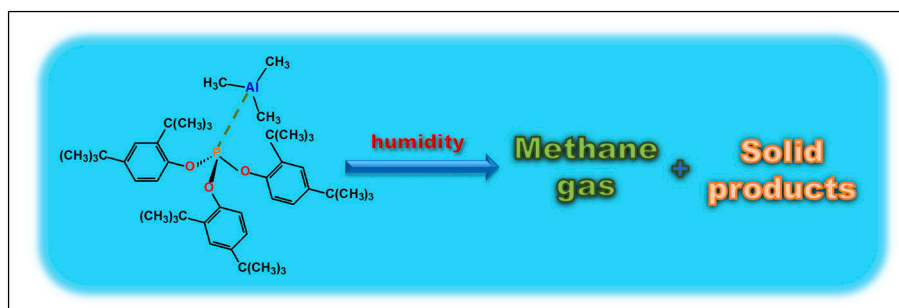
To identify the compound(s) potentially involved in the blistering process, we analyzed the isopropanol used to wash off the patches. Mass spectrometric investigation of eluted isopropanol revealed the unambiguous presence of a commonly used polyethylene antioxidant that has an excellent solubility in isopropanol [22], namely tris(2,4-di-tert-

butylphenyl)phosphite (CAS No.: 31570-04-4; common commercial names are Irgafos® 168, Alkanox® 240, Doverphos® S-480) occurring as protonated molecules (i.e., $[M + H]^+$) at m/z 647.457 (calculated monoisotopic m/z for the composition of $C_{42}H_{64}O_3P$ is 647.459) and its oxidized form at m/z 663.453 (calculated monoisotopic m/z for the composition of $C_{42}H_{64}O_4P$ is 663.454) (see Fig. 9) [23]. Antioxidant segregation is a common, well-known phenomenon in the polymer industry [24,25]. Furthermore, it is known that during film production, the additives, especially solid phosphite antioxidants tend to plate out on the rollers of the processing equipment. The built-up material can also transfer back to the produced film as particles [16]. This is another way the material responsible for blistering can end up on the surface of the polymer film.

3.9. Suggested process for the blister formation

Alumina is a great gas barrier [26], so the reactive substance (water or oxygen) must go through the polymer film to react with the bloomed component patches. This is confirmed by our experience that lifting the sample (fixed on the holder ring) from the ALD machine's sample tray and putting it back caused the start of bubble formation earlier, because in this case the back-side of the sample (uncoated face of the LDPE film) was exposed faster to the ambient, humid air. Without lifting the sample, the processing chamber's dry nitrogen is trapped under the holder ring, and the gas exchange for the ambient air is limited by the smoothness of the sample holder and the machine's sample tray.

All of these observations suggest that TMA is probably trapped in the bloomed component, water diffuses through the polymer, reacts with the trapped TMA, and the created methane forms bubbles between the alumina layer and the polyethylene film. However, plasma treatment breaks the bloomed material in both the physical and chemical sense, preventing the trapping of TMA. According to these findings, we propose that the TMA, which is considered to be a weak Lewis acid, and the Irgafos® 168 (Lewis base) react, and a portion of the reactive TMA is



Scheme 1. Reaction of the water with the TMA-Irgafos® 168 adduct.

retarded between the LDPE and the ALD layer. However, after exposure of the PE-ALD-coated LDPE foil to ambient air, the water vapor that diffused into the composite from the ambient air can react heavily with the retarded TMA molecules to form methane gas (CH_4), in addition to other solid products, as shown in Scheme 1. Hence, the gas formation results in blowing up the ALD layer and forming blisters.

3.10. Calculations to confirm the feasibility of the process

The sizes of the formed bubbles were within the same order of magnitude, with an estimated average diameter of approximately 300 μm and a height of 15 μm . To estimate the volume and mole number of the methane gas trapped by the bubble, we treated these bubbles as sections of a sphere, specifically as spherical caps, and applied eq. (1) for the volume calculations.

$$V = \frac{1}{6} \pi (3r^2 + h^2)h \quad (1)$$

Here, V , r , and h represent the volume, base radius and height of the spherical cap, respectively. Furthermore, assuming the trapped methane gas has pressure and temperature similar to the environmental conditions (i.e., $P = 10^5 \text{ Pa}$, $T = 25^\circ\text{C}$), the volume of the trapped methane is calculated to be $5.3 \times 10^{-10} \text{ dm}^3$, corresponding to $2.2 \times 10^{-11} \text{ mol}$. Additionally, it is estimated that approximately $7.2 \times 10^{-12} \text{ mol}$ TMA and $1.1 \times 10^{-11} \text{ mol}$ or $2 \times 10^{-10} \text{ g}$ of water were required to form $2.2 \times 10^{-11} \text{ mol}$ methane. According to the 1:1 Lewis complex formation shown in Scheme 1, $7.2 \times 10^{-12} \text{ mol}$ tris(2,4-di-tert-butylphenyl) phosphite was involved in the trapping process.

We can perform a simple sanity check on the suggested process by performing an estimation for the polymer film's water vapor transmission rate (WVTR) with one significant digit. During the growth, the average base radius of the bubble can be estimated as $8 \times 10^{-5} \text{ m}$ (half of the final radius). The amount of water vapor diffusing through this circle shaped area is $2 \times 10^{-10} \text{ g}$ over roughly 5 min, that is 300 s. From these, the water vapor transmission rate (WVTR) can be estimated as about 3 $\text{g/m}^2/\text{day}$ which is a very reasonable value for a 10 μm thick LDPE foil in a low relative humidity (20–40 %), room temperature environment [27]. Please note, that the other way how water can get to the TMA trapped between the polymer and the Al_2O_3 is through the oxide layer. However, the WVTR of a 50 nm thick Al_2O_3 grown by ALD is in the $10^{-4} \text{ g/m}^2/\text{day}$ range [28], so the water transmission via the oxide layer can be considered negligible.

4. Conclusion

This work reports a phenomenon where a 10 μm thick LDPE film, coated with a 50 nm thick Al_2O_3 layer using low-temperature PE-ALD, formed ultra-giant sized blisters (larger than previously reported) shortly after removal from the processing chamber. Upon investigation, we revealed that the reason for the blistering is the segregation (blooming) of an antioxidant component, tris(2,4-di-tert-butylphenyl) phosphite, from the LDPE. The evidence suggests the following mechanism: i) During the PE-ALD process, the segregated material entraps some TMA precursor. ii) After the deposition of the Al_2O_3 layer, the environmental humidity can diffuse through the LDPE layer from the unprocessed side and react with the trapped TMA. iii) The reaction produces methane gas that is trapped between the polymer and the Al_2O_3 layer causing the blistering.

The formation of blisters increases the stress in the Al_2O_3 layer and the bursting bubbles can cause a high number of cracks and also large area discontinuities in the layer, deteriorating its barrier properties. We showed that a 10 s plasma pre-treatment prevents the blister formation by altering the segregated material. Alternatively, washing the surface with isopropanol can remove the segregated material. We have found no reference of the described phenomenon in the scientific literature, the interactions between ALD precursors and polymer additives are rarely

investigated.

CRediT authorship contribution statement

János J. Tomán: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Eszter Baradács:** Writing – review & editing, Validation, Methodology, Investigation. **Gergő Vecsei:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis. **Lajos Nagy:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis. **Bence Parditka:** Validation, Methodology, Investigation. **Sándor Kéki:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Formal analysis, Conceptualization. **Zoltán Erdélyi:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus. This project was also supported by the University of Debrecen Program for Scientific Publication. G.V. was supported by the ÚNKP-23-3 New National Excellence Program of the Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund.

Data availability

Data will be made available on request.

References

- [1] A.E. Abusrafa, S. Habib, I. Krupa, M. Ouederni, A. Popelka, Modification of polyethylene by RF plasma in different/mixture gases, *Coatings* 9 (2) (2019), <https://doi.org/10.3390/coatings9020145>.
- [2] S. Gurusankar, G.M. Rao, M. Komath, A.M. Raichur, Plasma surface modification of polystyrene and polyethylene, *Appl. Surf. Sci.* 236 (1) (2004) 278–284, <https://doi.org/10.1016/j.apsusc.2004.04.033>.
- [3] T.O. Kääriäinen, P. Maydannik, D.C. Cameron, K. Lahtinen, P. Johansson, J. Kuusipalo, Atomic layer deposition on polymer based flexible packaging materials: growth characteristics and diffusion barrier properties, *Thin Solid Films* 519 (10) (2011) 3146–3154, <https://doi.org/10.1016/j.tsf.2010.12.171>.
- [4] H.B. Profijt, S.E. Potts, M.C.M. van de Sanden, W.M.M. Kessels, Plasma-assisted atomic layer deposition: basics, opportunities, and challenges, *J. Vac. Sci. Technol. A* 29 (5) (2011) 050801, <https://doi.org/10.1116/1.3609974>.
- [5] F. Zaera, The surface chemistry of thin film atomic layer deposition (ALD) processes for electronic device manufacturing, *J. Mater. Chem.* 18 (30) (2008) 3521–3526, <https://doi.org/10.1039/B803832E>.
- [6] J. Ott, et al., Impact of doping and silicon substrate resistivity on the blistering of atomic-layer-deposited aluminium oxide, *Appl. Surf. Sci.* 522 (2020) 146400, <https://doi.org/10.1016/j.apsusc.2020.146400>.
- [7] B. Iandolo, R.S. Davidsen, O. Hansen, Avoiding blistering in Al_2O_3 deposited on planar and black Si, *Sol. Energy Mater. Sol. Cells* 187 (2018) 23–29, <https://doi.org/10.1016/j.solmat.2018.07.014>.
- [8] R. Matsumura, N. Fukata, Direct detection of free H_2 outgassing in blisters formed in Al_2O_3 atomic layers deposited on Si and methods of its prevention, *ACS Appl. Mater. Interfaces* 14 (1) (2022) 1472–1477, <https://doi.org/10.1021/acsami.1c20660>.
- [9] H. Huang, et al., 20.8% industrial PERC solar cell: ALD Al_2O_3 rear surface passivation, efficiency loss mechanisms analysis and roadmap to 24%, *Sol. Energy Mater. Sol. Cells* 161 (2017) 14–30, <https://doi.org/10.1016/j.solmat.2016.11.018>.

- [10] B. Vermang, et al., On the blistering of atomic layer deposited Al₂O₃ as Si surface passivation, in: *2011 37th IEEE Photovoltaic Specialists Conference*, 2011, pp. 003562–003567, <https://doi.org/10.1109/PVSC.2011.6185916>.
- [11] R.L. Kovács, et al., Effect of nanoscopic defects on barrier performance of thin films deposited by plasma-enhanced atomic layer deposition on flexible polymers, *Thin Solid Films* 738 (2021) 138960, <https://doi.org/10.1016/j.tsf.2021.138960>.
- [12] H. Liu, S. Guo, R.B. Yang, C.J.J. Lee, L. Zhang, Giant blistering of nanometer-thick Al₂O₃/ZnO films grown by atomic layer deposition: mechanism and potential applications, *ACS Appl. Mater. Interfaces* 9 (31) (2017) 26201–26209, <https://doi.org/10.1021/acsami.7b08260>.
- [13] A. Bulusu, et al., Engineering the mechanical properties of ultrabARRIER films grown by atomic layer deposition for the encapsulation of printed electronics, *J. Appl. Phys.* 118 (8) (2015) 085501, <https://doi.org/10.1063/1.4928855>.
- [14] C.M. Small, G.M. McNally, W.R. Murphy, A. Marks, The manufacture and performance of polyethylene-Polyisobutylene films for cling applications, *Dev. Chem. Eng. Miner. Process.* 11 (1–2) (2003) 169–184, <https://doi.org/10.1002/apj.5500110217>.
- [15] A. Xu, S. Roland, X. Colin, Physico-chemical characterization of the blooming of Irganox 1076® antioxidant onto the surface of a silane-crosslinked polyethylene, *Polym. Degrad. Stab.* 171 (2020) 109046, <https://doi.org/10.1016/j.polymdegradstab.2019.109046>.
- [16] D. Stevenson, M. R. Jakupca, and N. Bersaglini, “Method for reducing plate-out of solid phosphites in polymers,” WO2010096757A1, Aug. 26, 2010 Accessed: Jan. 23, 2025. [Online]. Available: <https://patents.google.com/patent/WO2010096757A1/en>.
- [17] J. O. Osby, B. W. Walther, J. E. Ruiz, J. W. Hobson, and C. Serrat, “Polyethylene compositions having reduced plate out, and films made therefrom having reduced blooming,” US20130225738A1, Aug. 29, 2013 Accessed: Mar. 07, 2025. [Online]. Available: <https://patents.google.com/patent/US20130225738A1/en>.
- [18] D.M. Choi, C.K. Park, K. Cho, C.E. Park, Adhesion improvement of epoxy resin/polyethylene joints by plasma treatment of polyethylene, *Polymer* 38 (25) (1997) 6243–6249, [https://doi.org/10.1016/S0032-3861\(97\)00175-4](https://doi.org/10.1016/S0032-3861(97)00175-4).
- [19] N. Sprang, D. Theirich, J. Engemann, Plasma and ion beam surface treatment of polyethylene, *Surf. Coat. Technol.* 74–75 (1995) 689–695, [https://doi.org/10.1016/0257-8972\(95\)08340-5](https://doi.org/10.1016/0257-8972(95)08340-5).
- [20] F. Awaja, M. Gilbert, G. Kelly, B. Fox, P.J. Pigram, Adhesion of polymers, *Prog. Polym. Sci.* 34 (9) (2009) 948–968, <https://doi.org/10.1016/j.progpolymsci.2009.04.007>.
- [21] R.L. Kovács, et al., Surface characterization of plasma-modified low density polyethylene by attenuated total reflectance fourier-transform infrared (ATR-FTIR) spectroscopy combined with chemometrics, *Polym. Test.* 96 (2021) 107080, <https://doi.org/10.1016/j.polymertesting.2021.107080>.
- [22] M. Kolodziejski et al., “Solubility for Common Extractable Compounds,” Eurofins Scientific, Lancaster Laboratories. Accessed: Sep. 18, 2024. [Online]. Available: https://cdnmedia.eurofins.com/eurofins-us/media/1709957/solubility-for-common-extractable-compounds_elusa2019.pdf.
- [23] K. Fouyer, O. Lavastre, D. Rondeau, Direct monitoring of the role played by a stabilizer in a solid sample of polymer using direct analysis in real time mass spectrometry: the case of Irgafos 168 in polyethylene, *Anal. Chem.* 84 (20) (2012) 8642–8649, <https://doi.org/10.1021/ac301759q>.
- [24] B. Marcato, S. Guerra, M. Vianello, S. Scalia, Migration of antioxidant additives from various polyolefinic plastics into oleaginous vehicles, *Int. J. Pharm.* 257 (1–2) (2003) 217–225, [https://doi.org/10.1016/s0378-5173\(03\)00143-1](https://doi.org/10.1016/s0378-5173(03)00143-1).
- [25] N. Médard, et al., Antioxidant segregation and crystallisation at polyester surfaces studied by ToF-SIMS, *Appl. Surf. Sci.* 203–204 (2003) 571–574, [https://doi.org/10.1016/S0169-4332\(02\)00768-7](https://doi.org/10.1016/S0169-4332(02)00768-7).
- [26] K.L. Jarvis, P.J. Evans, A. Nelson, G. Triani, Comparisons of alumina barrier films deposited by thermal and plasma atomic layer deposition, *Mater. Today Chem.* 11 (2019) 8–15, <https://doi.org/10.1016/j.mtchem.2018.10.002>.
- [27] G.L. Robertson, *Food Packaging: Principles and Practice*, Third Edition, 3rd ed., CRC Press, Boca Raton, 2016 <https://doi.org/10.1201/b21347>.
- [28] T. Nam, et al., Moisture barrier properties of low-temperature atomic layer deposited Al₂O₃ using various oxidants, *Ceram. Int.* 45 (15) (2019) 19105–19112, <https://doi.org/10.1016/j.ceramint.2019.06.156>.