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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Low-Temperature, Ultra-Giant Blistering of Atomic Layer Deposited Barrier Coatings on Polymer Films Caused by Additive Segregation

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(Received: 2025/11/11, Published online: 2025/11/13)

Plasma-enhanced atomic layer deposition (PE-ALD) at low temperatures is an advanced technique for coating flexible polyolefin polymers like low-density polyethylene (LDPE) to enhance their barrier properties for moisture and gases. The ALD process is highly dependent on surface preparation, and LDPE presents challenges due to its non-polar nature. In this study, we demonstrate how polymer additive segregation at the surface (known as blooming) can undermine the effectiveness of these barrier coatings. When a 10 μm LDPE film was coated with a 50 nm Al_2O_3 layer via low-temperature PE-ALD, ultra-giant blisters - larger than previously reported - formed within minutes of exposure to ambient conditions. The evidence [1] suggests the following mechanism, see Fig. 1: 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, see Fig. 2, can cause a high number of cracks and also large area discontinuities in the layer, deteriorating its barrier properties. We showed that a 10 second 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.

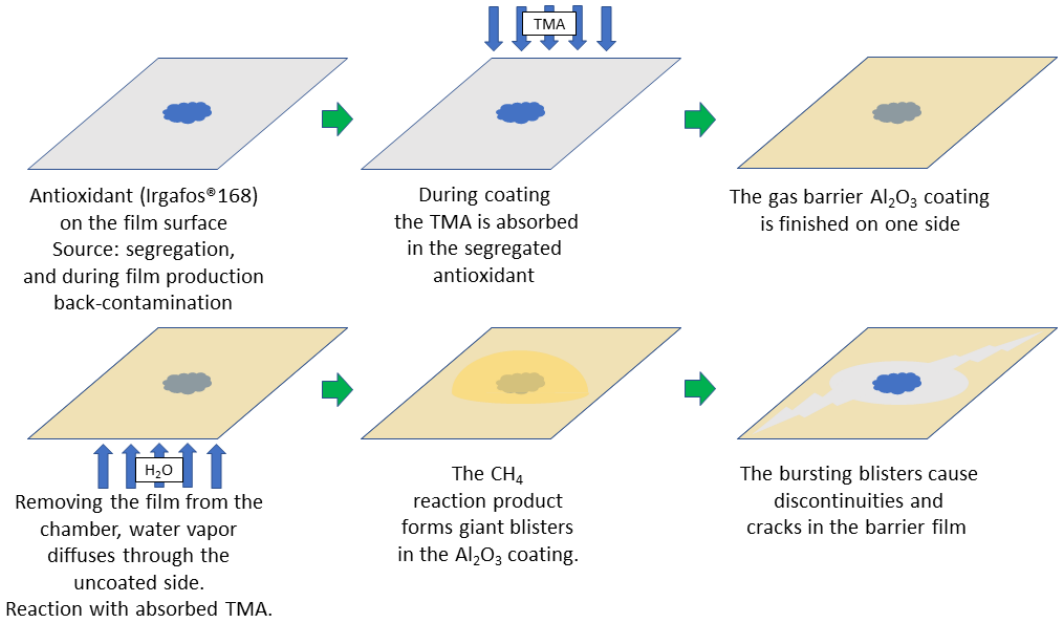

Fig. 1. Suggested process of ultra-giant blister formation.

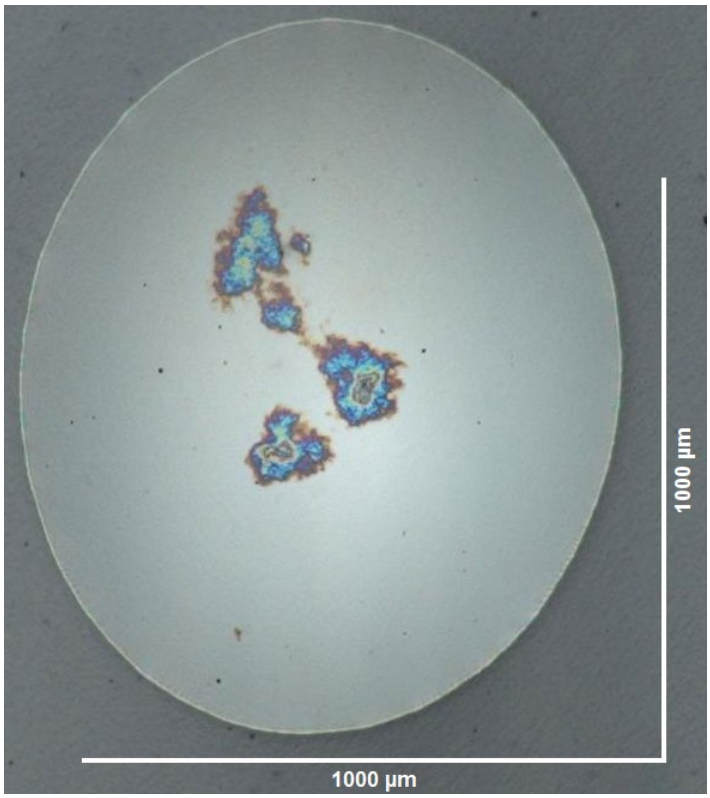

Fig. 2. Bright field optical microscope image of one of the largest bubbles. Scale bars are 1 mm long. The colorful patches are the bloomed component.

Acknowledgements

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.

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