Surface modification of biodegradable polymers by low temperature plasma for improving their performances as food packaging

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Biodegradable polymers are viewed as a promising eco-friendly solution to replace conventional plastic polymers as packaging materials, reducing the enormous environmental impact that the latter involve [1]. However, biodegradable plastics still occupy a rather restricted section of the plastic food packaging market due some limitations including their poor gas barrier and UV protection properties [2]. In fact, both oxygen and UV light lead to oxidation processes which alter food quality and produce toxic compounds [3,4]. In this regard, low temperature plasma technique can be exploited to fabricate multifunctional polymeric surfaces with significant enhanced performances. This approach is completely environmentally friendly avoiding the use of toxic solvents or high temperatures that could damage the polymer structure [5,6] and it is crucial to extend the use of biodegradable packaging and preserve the food quality. In this work we report on surfaces modifications of two commercial biodegradable polymers by low temperature plasma processes. In particular, tungsten oxide (WO_x) thin films were deposited by plasma magnetron sputtering on poly(lactic acid) (PLA) in order to enhance its performances in terms of barrier to oxygen and UV light protection. The coated samples are characterized by an oxygen permeability and light transmittance in the UV-B region reduced of ≈ 90% compared to pristine PLA. Finally, plasma etching was employed to tailor the surface morphology of poly(butylene succinate) (PBS) resulting in a packaging with antimicrobial effect due to the nature inspired contact-killing mechanism. The treated samples showed excellent antimicrobial activity against 4 different types of bacteria, i.e., *Escherichia coli, Pseudomonas fluorescens, Listeria innocua and Staphylococcus aureus*, with a reduction greater than 5 $\log_{10}$ CFU cm^{-2} after 24 h.

[1] Han, J.W.; Ruiz-Garcia, L.; Qian, J.-P.; Yang, X.-T. Food Packaging: A Comprehensive Review and Future Trends. Compr. Rev. Food Sci. Food Saf. **2018**, 17, 860.
[2] Wu, F.; Misra, M.; Mohanty, A.K. Challenges and New Opportunities on Barrier Performance of Biodegradable Polymers for Sustainable Packaging. Progress in Polymer Science **2021**, 117, 101395.
[3] Shahabi-Ghahfarrokhi, I.; Khodaiyan, F.; Mousavi, M.; Yousefi, H. Preparation of UV-Protective Kefiran/Nano-ZnO Nanocomposites: Physical and Mechanical Properties. Int. J. Biol. Macromol. **2015**, 72, 41.
[4] Llorens, A.; Lloret, E.; Picouet, P.A.; Trbojevich, R.; Fernandez, A. Metallic-Based Micro and Nanocomposites in Food Contact Materials and Active Food Packaging. Trends Food Sci. Technol. **2012**, 24, 19.
[5] Ma, C.; Nikiforov, A.; De Geyter, N.; Dai, X.; Morent, R.; Ostrikov, K. (Ken) Future Antiviral Polymers by Plasma Processing. *Progress in Polymer Science* **2021**, *118*, 101410.
[6] Pankaj, S.K.; Bueno-Ferrer, C.; Misra, N.N.; Milosavljević, V.; O'Donnell, C.P.; Bourke, P.; Keener, K.M.; Cullen, P.J. Applications of Cold Plasma Technology in Food Packaging. Trends in Food Science & Technology **2014**, 35, 5.