## Phytochemicals as inhibitors of polylactide's photooxidation and thermooxidation



Economic development and increasing environmental social awareness related to massive amounts of plastic waste drive the industry towards looking for environmentally friendly materials like sustainable polymers. Despite the majority of the public's stated desire to use green polymers, their inferior performance and higher costs are still obstacles to increasing their actual market share. The most commonly used biopolymer is polylactide (PLA), a compostable material made from renewable resources, applied in disposable products, agricultural and medicinal applications, and 3D printing. PLA can be produced from two different compounds, lactide, and lactic acid, each of which comes in two varieties differing in chirality – a structural property resulting from the mutual spatial arrangement of individual atoms in the molecule. As a result, PLA exists in varieties with different structural features, which affects its properties.

One of the PLA drawbacks is susceptibility to oxidation, which deteriorates its mechanical performance and causes discoloration. The oxidation process can be induced by temperature (thermooxidation) or UV irradiation (photooxidation), and its general mechanisms for PLA are currently known. However, researchers have not investigated the oxidation of different grades of PLA, so the influence of its chirality, as well as other structural parameters, on the oxidation process has been overlooked.

The issue of PLA susceptibility to oxidation is real, and different modifiers are applied to overcome it. Following pro-environmental trends and the Circular Economy concept, it is beneficial to modify plastics with renewable or recycled raw materials. Multiple natural materials, including wastes from the agricultural or food industry, like citrus peels, coffee husks, or hops, contain numerous phytochemicals. Due to the antioxidant activity, their presence may be beneficial for polymers, including PLA. Among them are compounds treated as natural preservatives or anti-aging agents in cosmetics, like caffeine,  $\beta$ -carotene, and vitamins C and E. Modes of action of various phytochemicals are quite different, so it is important to analyze their impact on PLA resistance to oxidation.

Staying close to the environmental issues of biopolymers and keeping in mind the above-mentioned pollution, it is crucial to provide methods for PLA recycling or disposal. This material can be reused after mechanical recycling. However, it often results in deterioration of its performance. The application of phytochemicals may provide a solution to this problem. It can also be subjected to chemical recycling, yielding primary raw materials for manufacturing PLA or other plastics, but the impact of phytochemicals on the process and properties of final products has to be comprehensively assessed. Moreover, PLA can be utilized by composting, which involves material decomposition caused by microorganisms. Phytochemicals, except antioxidant activity, may also act as antimicrobials. Therefore, their application should be adjusted so as not to impede the composting, which would be environmentally unfavorable.

Considering the aspects mentioned above, understanding the impact of the PLA structural parameters on the mechanism of its photooxidation and thermooxidation requires a comprehensive study evaluating different PLA grades under the same conditions and providing detailed information. Such a study is proposed in the presented project, and its results would enable extending the knowledge of PLA.

The presented project aims to fill the current knowledge gaps by analyzing the influence of PLA structural parameters on its oxidation mechanism and matching the material's needs with the mode of action of particular phytochemicals. To achieve this, films based on various PLA grades, differing in structural parameters, and modified with phytochemicals will be prepared by the solution casting method, which involves dissolving the material in a solvent followed by its evaporation. The appearance, physical and chemical structure, processing, mechanical and thermal properties of films, and changes caused by thermooxidation or photooxidation will be assessed. Obtained information would be vital for future PLA applications and the proper selection of its modifiers. It would enable the efficient application of waste-based materials, which could act as active fillers.

The project would analyze the phytochemicals' impact not only on the oxidation resistance but also on the recycling and composting of PLA. Prepared materials would be subjected to production-use-recycling cycles and composting tests. In the first case, cycles will comprise the primary processing operations (production), accelerated aging simulating the consumer use of the material, and recycling operations. Composting tests will be performed to simulate the industrially applied process of PLA disposal. Obtained results would enable the proper selection of modifiers, enhancing the PLA performance and stability during recycling cycles without impeding its disposal via composting.

The **PHYT4PLA** project addresses issues related to PLA use, recycling, and disposal. It could be the answer to today's challenges related to the utilization of plastic and food waste. In the future, the obtained results could broaden the PLA application range, contributing to the inhibition of unfavorable environmental changes and improving the standard of living on a global scale.

