Biodegradation and synthesis of plastics using selected enzymes and microorganisms

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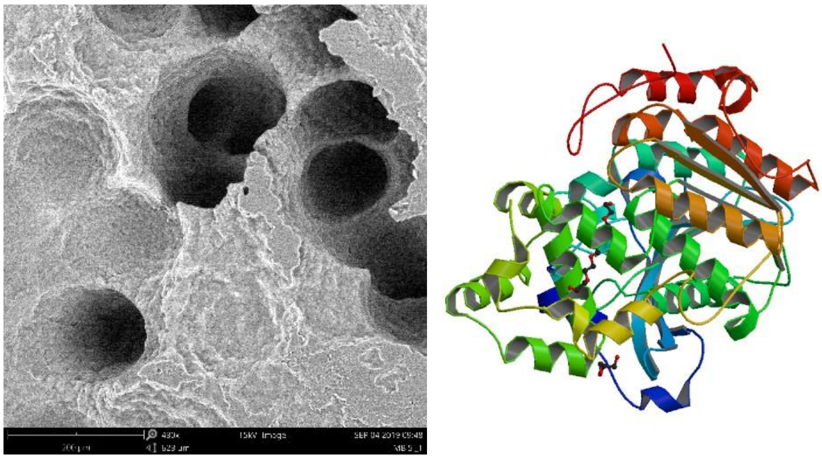
Thanks to the advantages of plastic materials, their use has steadily increased last decades due to their enhanced properties. This fact is reflected in global polymer production, which amounted to 359 million tonnes in 2018, a 3.2% increase over the previous year. Bioplastics currently represent only 1% of all plastics produced annually, but demand is on the rise, given the many options for diversification due to the emergence of increasingly more sophisticated applications and products. According to the latest market research by European Bioplastics, in cooperation with Nova-Institute, global bioplastic production capacity is expected to grow from 2.11 million tonnes in 2019 to 2.43 million by 2024.

However, one of the greatest challenges to face associated with the use of plastics is environmental pollution if they are not managed properly. Because most plastics have very low biodegradation rates, they accumulate in the environment at the end of their shelf life. Many plastics also end up in landfills, since no methods are currently available for proper waste treatment and recycling. This is particularly truefor multilayer materials, given that mechanical recycling is not effective at separating the layers, which means these materials are considered non-recyclable. It is also the case of plastics that acquire the organoleptic properties of the product they contain, thus preventing subsequent recycling. It is, therefore, necessary to find alternative solutions in line with the circular economy strategy.

One of the research lines of the ENZPLAST2 project involves developing new recycling technologies that degrade the middle adhesive layers of multilayer materials so that the other layers can be easily classified and recycled.

These new biotechnology methods are based on the isolation of microorganisms capable of biodegrading specific types of polymers. Biodegradation of plastics involves two steps: binding of microorganisms to the polymer surface and growth of these microorganisms using the polymer as a source of carbon, followed by final polymer degradation into CO_2 and water under aerobic conditions, and biogas and water under anaerobic conditions. To carry out biodegradation, microorganisms produce and secrete enzymes into the environment that break down the polymer chain into low-molecular-weight fragments such as oligomers and monomers. The direct use of these specific enzymes is therefore another alternative for breaking down polymers. The monomers obtained as a product of the degradation reaction can be recovered and used to synthesize new products, thus making it a sustainable chemical recycling method.

The project's preliminary results point towards possible options for applying and implementing these technologies, given that certain isolated microorganisms have been used to degrade 70% of a polyurethane film (Figure 1a). Likewise, limiting stages for polymer degradation have been identified, such as oxygen transfer, that could help improve the performance of these systems. In addition, the application of enzymes to carry out polymer degradation using bio-based catalysts was assessed with positive results. More specifically, the activity of lipases, proteases and esterases was individually evaluated. Possible synergies that may occur between the different enzymes were also analysed and positive results were obtained for the joint activity of lipases and proteases and lipases and esterases.



a) **b)**

Figure 1. a) The surface of a polyurethane film after microbial degradation; b) Three-dimensional structure of the *Candida Antarctica* lipase A enzyme.

The use of microorganisms was also studied to eliminate odours from dairy packaging. The results show a significant reduction in the odour intensity of materials exposed to microorganisms compared to those not exposed to microbial action.

Once these recycling protocols are optimized, they will be validated in the industrial sector, especially by recycling companies, which will analyse the purity of waste flows for obtaining high-quality recycled materials and the industrial feasibility of the proposed methods.

Due to expansion of the global bioplastics market, which is expected to show six-fold growth[1], the ENZPLAST2 project will use enzymes to obtain polyester bioplastics, such as polybutylene succinate (PBS), polyethylene furanoate (PEF), polylactic acid (PLA), poly(butyl fumarate) (PBF) and poly(butylene adipate) (PBA). These polymers have applications in medicine and packaging.

The results indicate that lipase B (CalB) reactivity changes considerably depending on the polymeric support used for immobilization, as well as the immobilization method applied, i.e. covalent bonding or adsorption. Factors such as pore size, particle size and surface area of the polymer matrix are key when studying synthesis of these polyesters. It was also observed that the length of the diol chain used in the reaction affects the length of the resulting polymer chain. This confirms the high selectivity shown by enzymes when they are used as sustainable catalysts. This represents an advantage over the use of metal catalysts, which have associated certain toxicity, thus limiting their application in the biomedical industry, among others. Also of note is that enzyme synthesis processes consume much less energy, given that the optimal working temperature of enzymes is 25-95ºC compared to 180-230ºC, the temperature range used in conventional reactions for obtaining these polymers.

Finally, the incorporation of enzymes supported in cast plastics is being evaluated to improve their compostability. To this end, lipase B (CalB) was immobilized on polymeric and silicon substrates and dispersed in PLA and polyurethane (PU) under different conditions. Critical parameters in this analysis include preserving thermal stability of the final polymer and obtaining homogeneous enzyme distribution. The reduction of a product's biodegradation time with and without the enzyme will indicate if compostability has been improved.

In summary, the research done by the ENZPLAST2 project confirms the technical feasibility of the application of enzymes in the plastics sector, which means that their use can be encouraged among polymer manufacturers, recyclers and waste managers.

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[1] https://www.european-bioplastics.org/market/

AIMPLAS, the Plastics Technology Centre, is developing the ENZPLAST2 project, supported by the Valencian Institute of Business Competitiveness (IVACE), which aims to develop new, more sustainable processes for the production, recycling and composting of plastics through the use of enzymes and microorganisms.

AIMPLAS is participating in this project and carrying out research on this topic to meet its commitment to environmental sustainability. As a result, companies in the sector will be able to integrate circular economy criteria into their business models and turn the legislative changes that affect them into opportunities to improve efficiency and profitability and reduce environmental impact. AIMPLAS also does research in areas such as recycling, biodegradable materials and products, and the use of biomass and CO_2.