Advancements in biodegradable polymer circularity: bioproduction of monomers to developing biodegradation testing methods

by

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ABSTRACT

The environmental impact of plastics extends across their entire lifecycle, yet most efforts to improve their sustainability address individual stages — monomer synthesis, polymerization, or end-of-life management — in isolation. This thesis develops and applies experimental, computational, and engineering tools across multiple stages of biodegradable polymer lifecycles, connecting bio-based monomer production and polymerization to the microbial processes that ultimately determine a material's environmental fate.

Characterizing microbial degradation, however, is often limited by low-throughput assays, narrow organism panels, and limited insight into the enzymes responsible. Addressing these gaps requires tools that span experimental screening, automated measurement, and computational discovery. Existing high-throughput biodegradation methods were expanded to accommodate taxonomically diverse organisms through modified clear-zone assay conditions. This method was used to characterize the degrading potential of a panel of bacteria and fungi against commercial polymers and evaluate the biodegradability of acrylate–lipoic acid copolymers. To accelerate standardized testing, a fully automated biodegradation testing device was developed to monitor the degradation of 490 samples simultaneously, using novel image extraction methods to quantify degradation rate. This device was used to create optimized consortia for mixed plastic waste degradation, targeting specific polymers through consortia modifications, and was deployed to the Amazon basin where three novel PHB-degrading consortia were identified from environmental isolates. Using large-scale metagenomic analysis tools, a pan-genome analysis was performed across 452 species to reveal over 17,000 candidate depolymerases. Phylogenetic distance and ESM-2 protein language model embeddings were used to predict activity and rank candidates against experimentally validated depolymerases. Transcription factor enrichment analysis revealed the association of quorum sensing, biofilm formation, and hypoxia-related regulatory patterns with predicted depolymerases, suggesting a genetic basis for commonly reported degradation behavior.

Beyond end-of-life behavior, the upstream stages of polymer synthesis — monomer production and polymerization — equally shape a material's environmental footprint and downstream fate. An often-overlooked aspect of biodegradable polymer synthesis is the effect that residual synthesis components can have on downstream degradation. In particular, the toxic effects of tin-based catalysts on polymer biodegradation were investigated. The magnitude of inhibition was found to be both ligand- and species-dependent. In polymer samples, inhibition of biodegradation was observed at residual catalyst concentrations as low as 1 mol%. To address sustainable monomer production, a pathway for medium-chain α,ω-alkanediols was constructed, utilizing fatty acid biosynthesis with thioesterase modification for chain-length control. Octanoic and dodecanoic acid were successfully produced and, through the expression of a carboxylic acid reductase system, were further reduced to the corresponding alcohols. Additional engineering of terminal monooxygenase expression could enable future production of the target diols.

Spanning material science, metabolic engineering, and automation, this thesis addresses challenges at each stage of the biodegradable polymer lifecycle: monomer production, polymerization, and biodegradation. Combined, this work provides a framework for full consideration of polymer circularity in the development of sustainable biodegradable materials.

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