Reviving mixed plastic waste through chemoenzymatic recycling

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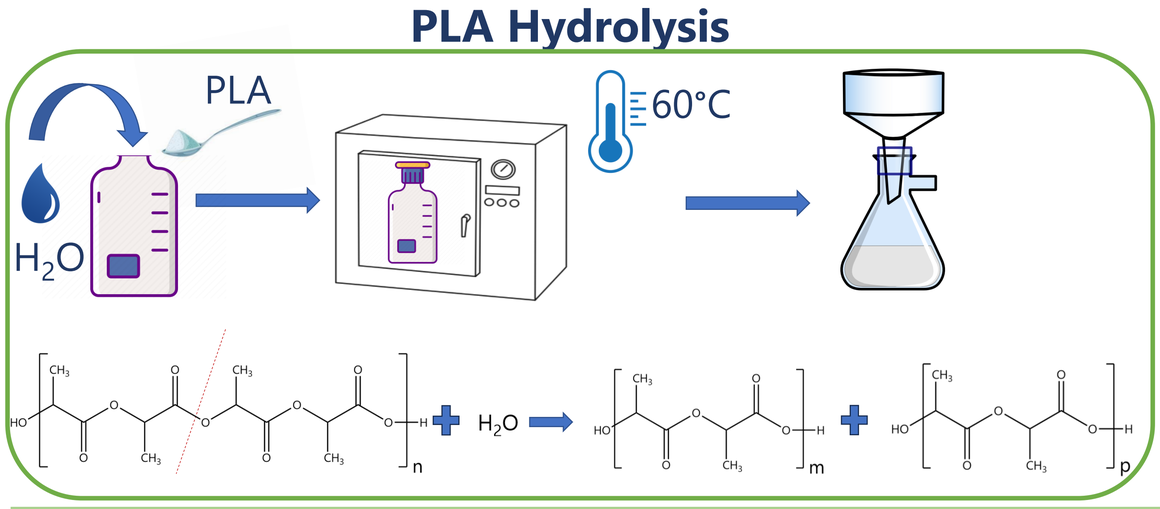
Introduction

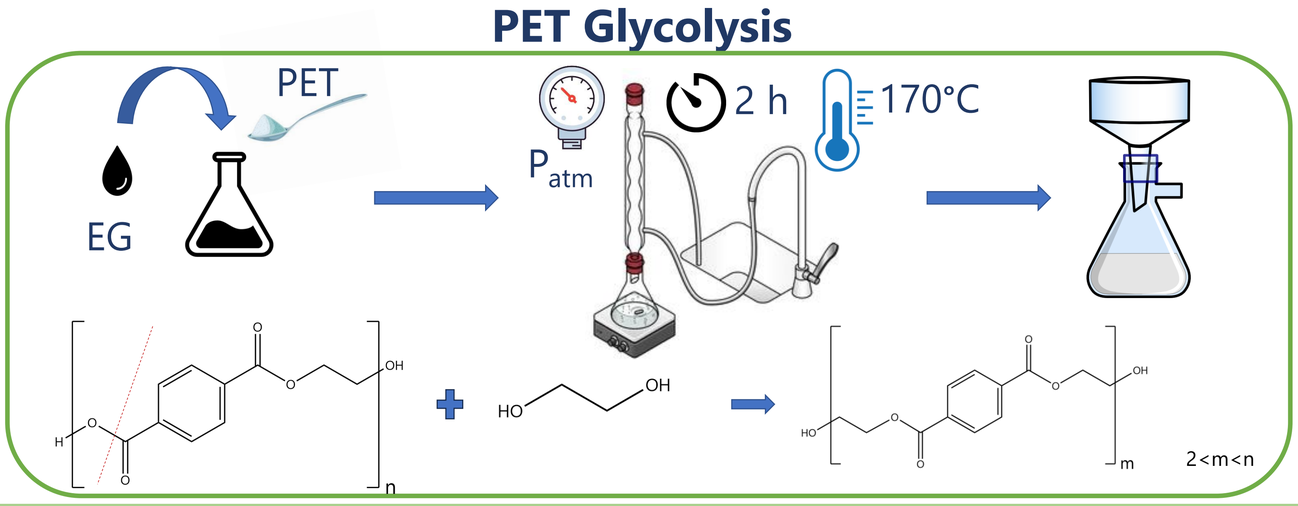
Poor **waste management** worldwide leads to constantly increasing environmental pollution; if current production and waste management trends continue, roughly 12bn tonnes of plastic waste are expected to end up in landfills or the natural environment by 2050. The main obstacle to viable mechanical recycling is the presence of different polymer types in end products (**mixed-plastic waste**), hampering the recycling process and reducing the recyclates' quality (downcycling). The ***EnZyReMix*** project aims to develop innovative methodologies, including **selective enzymatic degradation**, to separate complex packaging waste streams, i.e., mixed plastics, and valorise the depolymerized oligomers from post-consumer materials *via* upcycling approaches. Specifically, we focus on **mixtures of PLA/PET** since PLA is a new source of **polymeric contamination for rPET**, and their separation is not easily feasible due to their similar appearance and densities. In the first part of the research, commercially available PLA and PET grades have been submitted to ***solvolysis*** to prepare oligomers of controlled characteristics, including molecular weight, that will be used as induction media for the secretion of PLA and PET specific enzymes from target fungal strains through proteomics analyses, as well as substrates for co-crystallization studies.

Experimental Part

PLA Hydrolysis

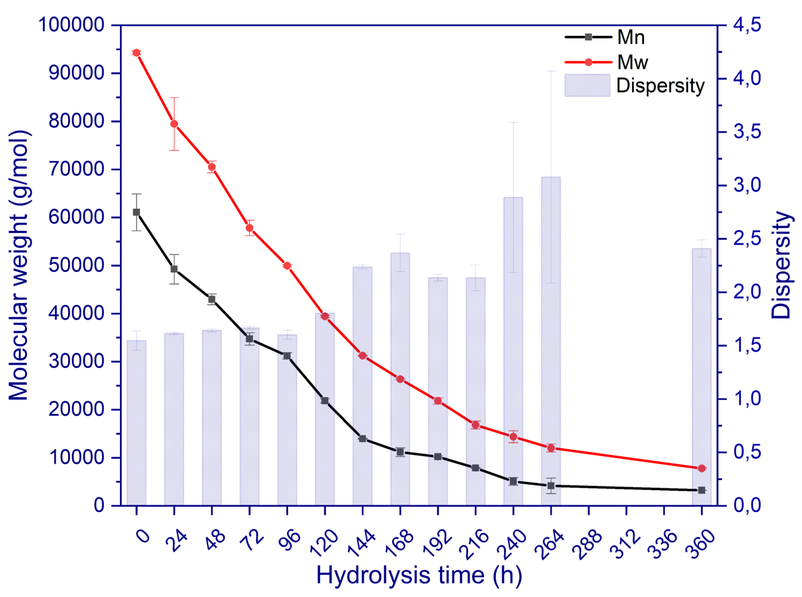


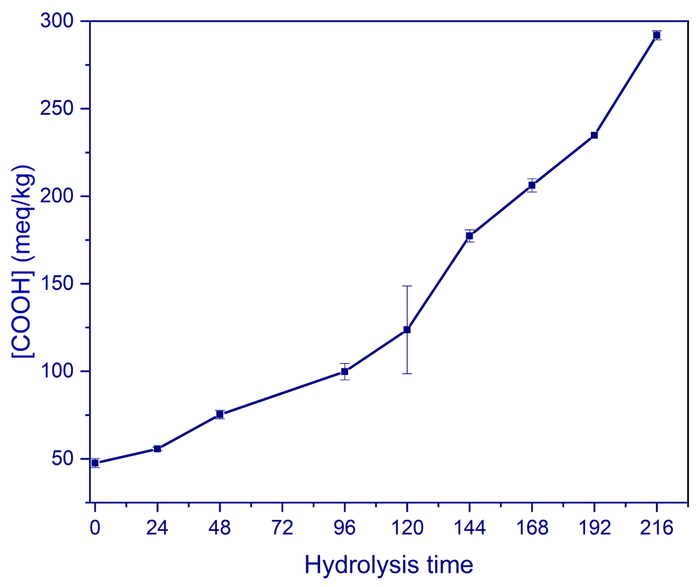
PET Glycolysis



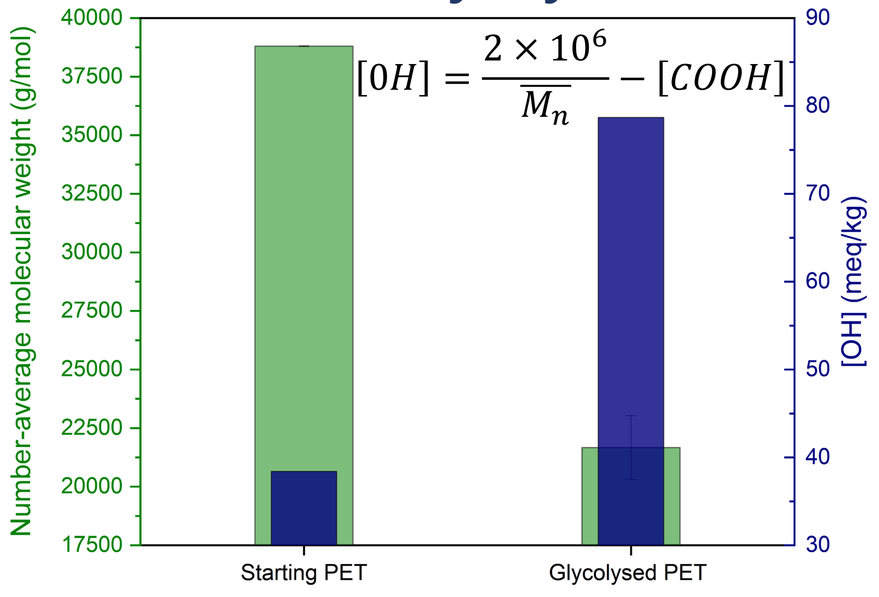
Results and Discussion

PLA Hydrolysis





PET Glycolysis



Power-of-the-time model

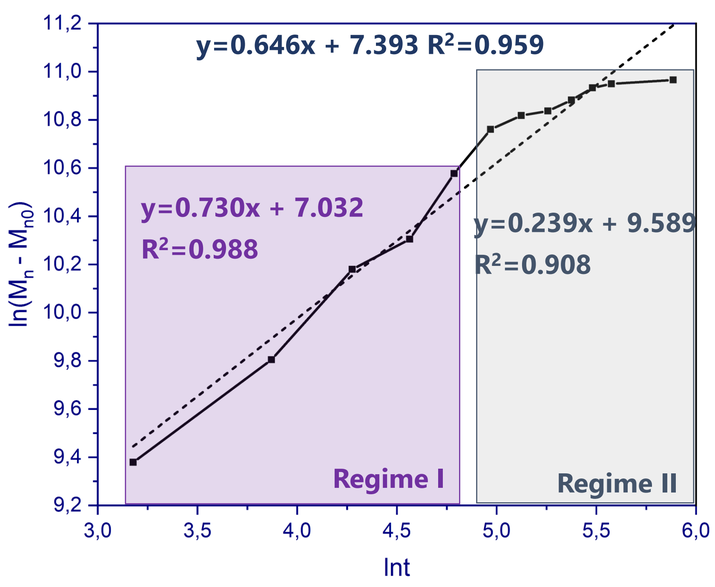
$$\ln(M_n - M_{n_0}) = \ln\left(\frac{k}{n+1}\right) + (n+1)\cdot\ln t$$

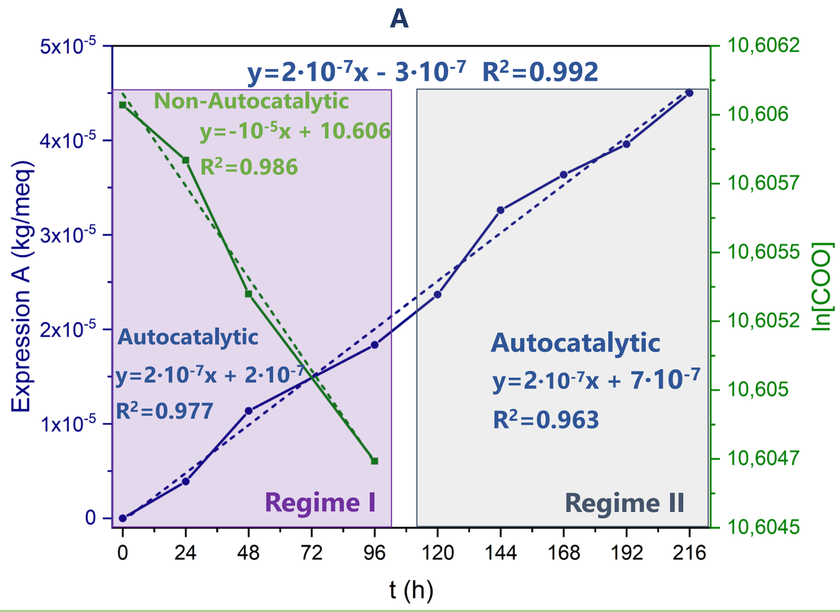
Flory theory-based autocatalytic and non-autocatalytic models

$$\frac{1}{[COO]_0 + [COOH]_0} \cdot \ln\frac{([COOH]_0 + u_t)([COO]_0)}{([COOH]_0)([COO]_0 - u_t)} = k \cdot t$$

(A)

$$\ln([COO]_t) = \ln([COO]_0) - k \cdot t$$





Rate constant calculations

k_{mean} [kg/meq·h]	$2.06 \cdot 10^{-7} \pm 11\%$
k_{plot} [kg/meq·h]	$2.12 \cdot 10^{-7}$, R^2 0.992
ΔS^2 [(kg/meq·h)²]	$1.71 \cdot 10^{-17}$

- **Low values** of the **deviation** between k_{mean} and k_{plot} indicating a **good model fit**
- The defined rate constant is similar to hydrolysis rate constants derived from **other autocatalytic models** in the **same hydrolysis conditions** (60°C) reported in the open literature:
  - ✓ k_{plot} **$2.12 \cdot 10^{-7}$ kg/meq·h** = **$4.10 \cdot 10^{-3}$ L/mol·day**
  - ✓ $k_{literature}$=**$7.42 \cdot 10^{-3}$ L/mol·day** (Mitchell *et al.* 2014)

Conclusions

Solvolysis was found effective in producing PLA and PET oligomers for the following plastic-converting enzymes' structure-function relationship studies, and as inducers for Secretomics studies. The fitting of the hydrolysis results to the examined models was found sufficient (R^2 > 0.95) providing a valuable tool to prepare oligomers of controlled characteristics. When submitted to a mild glycolysis process (short reaction time, temperature < 200 °C, no catalyst used) PET presented a significant MW decrease (ca. 45%) and OH-end group concentration increase (ca. 50%).

Acknowledgement

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