Chemical modification of enzymes for enhanced biocatalytic degradation of plastics in ionic liquids

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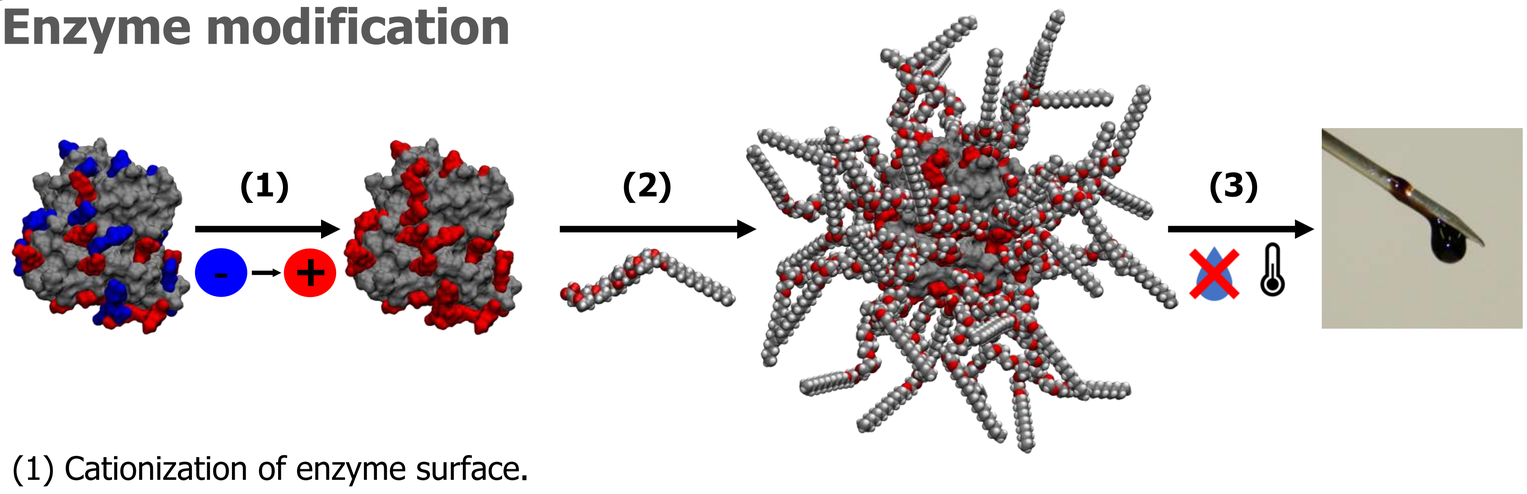
Introduction

Enzymes can perform many industrially relevant reactions with high specificity and efficiency. Recent successes in engineering have significantly broadened substrate scope. Despite this, effective enzyme-based biocatalysis largely remains limited by the aqueous solubility of substrates.

Ionic liquids are highly versatile solvents with tuneable and widely favourable properties. Particularly, ionic liquids can solvate a much larger range of substrates than conventional solvents, including otherwise recalcitrant polymers such as those involved in plastic production.

Here, we present a general chemical modification strategy to **unlock new reactivities of enzymes towards polymeric materials** through ionic liquid reaction design. In doing so, we provide a blueprint for facile depolymerisation of plastics.

Enzyme modification

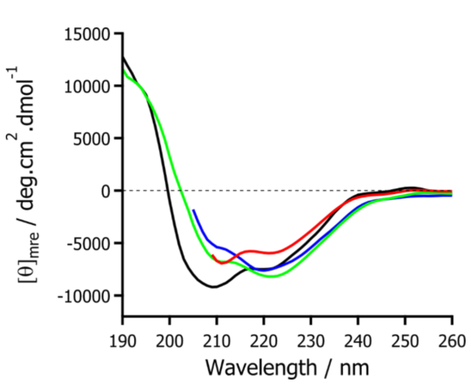


(1) Cationization of enzyme surface.

(2) Nanoconjugate formation *via* electrostatic complexation with anionic surfactants.

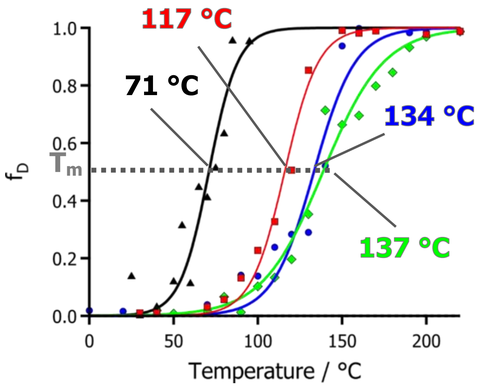
(3) Lyophilization and annealing to form solvent-free liquid enzyme.

Enzymes stabilized and enhanced in ionic liquids



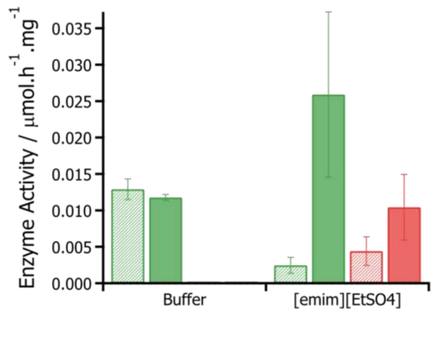
Key: **Aqueous**, **[bmpyrr][OTf]**, **[bmpyrr][NTf_2]**, **[bmpyrr][OAc]**

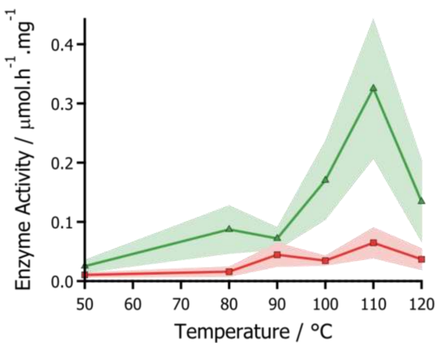
Glucosidase

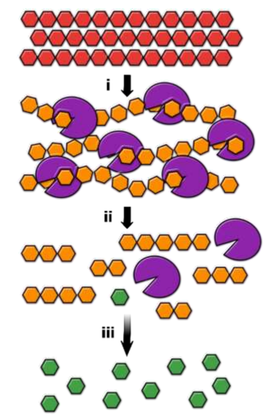


- Chemical modification maintains enzyme structure in ionic liquids.
- Thermal stability drastically improved after modification and in ionic liquids.

Substrates: **Cellobiose** **Cellulose**

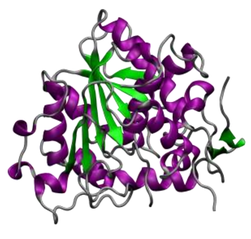




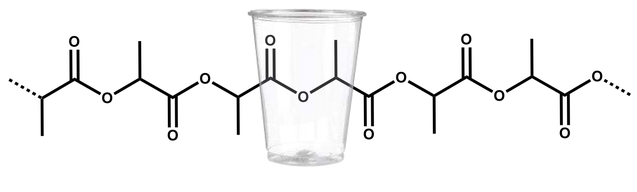


- Ionic liquid unlocks unseen reactivity of modified glucosidase towards cellulose.
- Optimum operating temperature shifts to 110 °C with 30x increase in activity.

Biocatalytic plastic depolymerisation



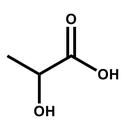
Lipase (CaLB)



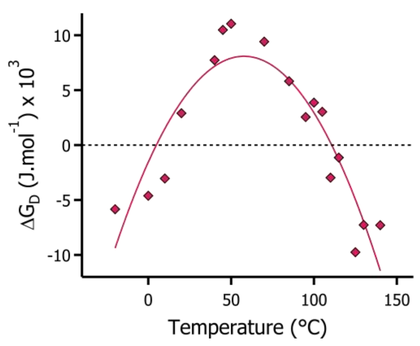
Poly(lactic acid)

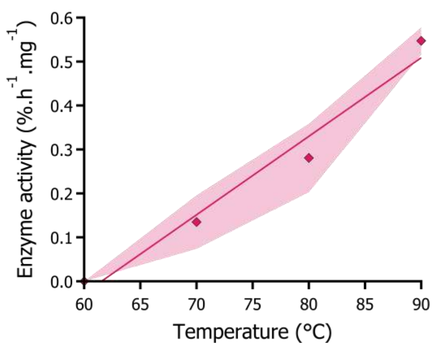
Ionic liquid

$T > T_g$



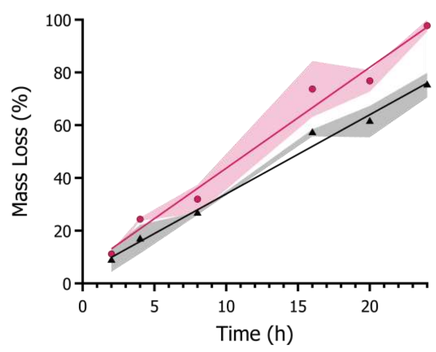
Lactic acid

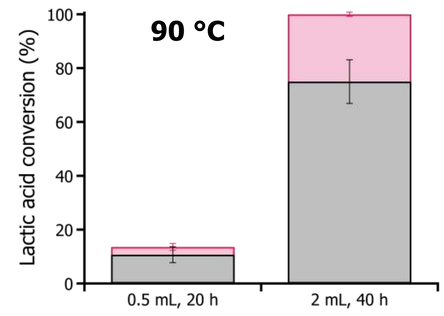


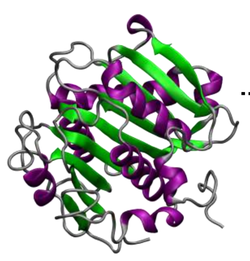


- Enzyme stabilization strategy shown on a range of enzymes, all active in ionic liquids at high temperatures.
- Modified lipase in [emim][OAc] can degrade PLA within 24 h with full depolymerisation within 40 h.
- Similarly, ongoing work is showing that cutinase in ionic liquids can degrade PET and α-chymotrypsin can degrade Nylon.
- Future work will screen more enzymes in a broader range of ionic liquids and conditions.

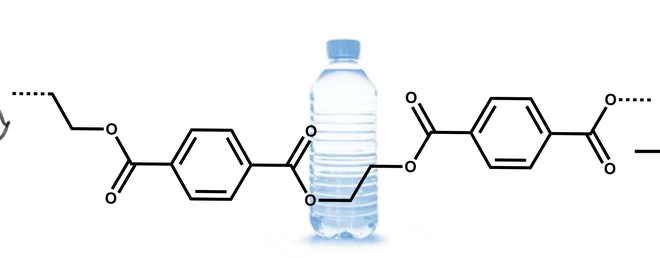
Key: **[emim][OAc]**, **[emim][$EtSO_4$]**, **Enzyme + IL**







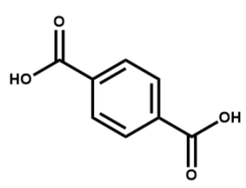
Cutinase



Poly(ethylene terephthalate)

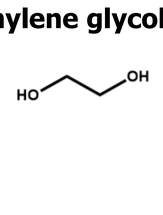
Ionic liquid

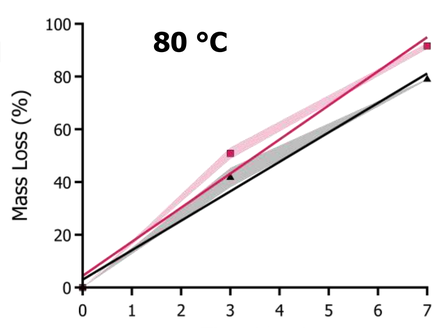
$T > T_g$

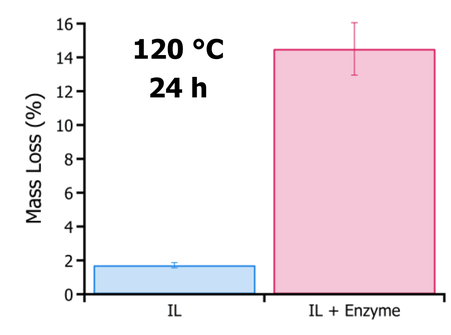


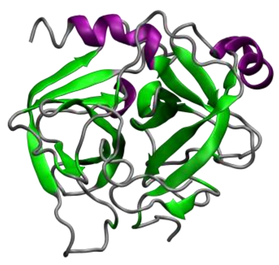
Terephthalic acid

Ethylene glycol

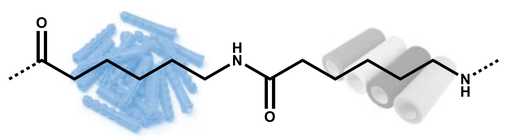








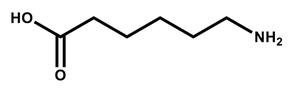
α-chymotrypsin



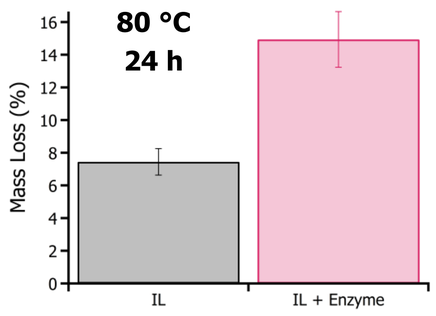
Nylon 6

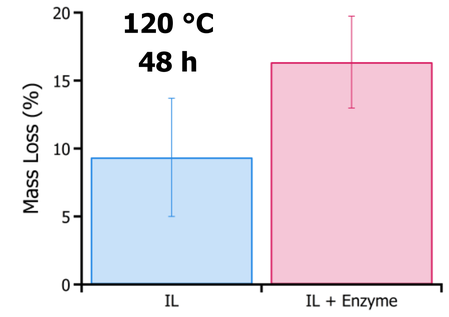
Ionic liquid

$T > T_g$



Aminocaproic acid





Conclusions

Chemical modification of enzymes to yield solvent-free liquids have shown to be a robust methodology for stabilizing enzymes against temperature and non-aqueous environments. Here, solubilizing stabilized enzymes in ionic liquids has been shown as a blueprint for significantly enhancing hydrolytic enzymes for plastic recycling.

In particular, we have shown that chemical modification of the ubiquitous enzyme lipase allows for highly efficient depolymerisation of post-consumer PLA. Furthermore, ongoing work shows how this approach can also be applied to a cutinase and α-chymotrypsin for the degradation of PET and Nylon, respectively.

References

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