Biocatalytic degradation of poly(lactic acid) to monomers using a chemically modified lipase in ionic liquids

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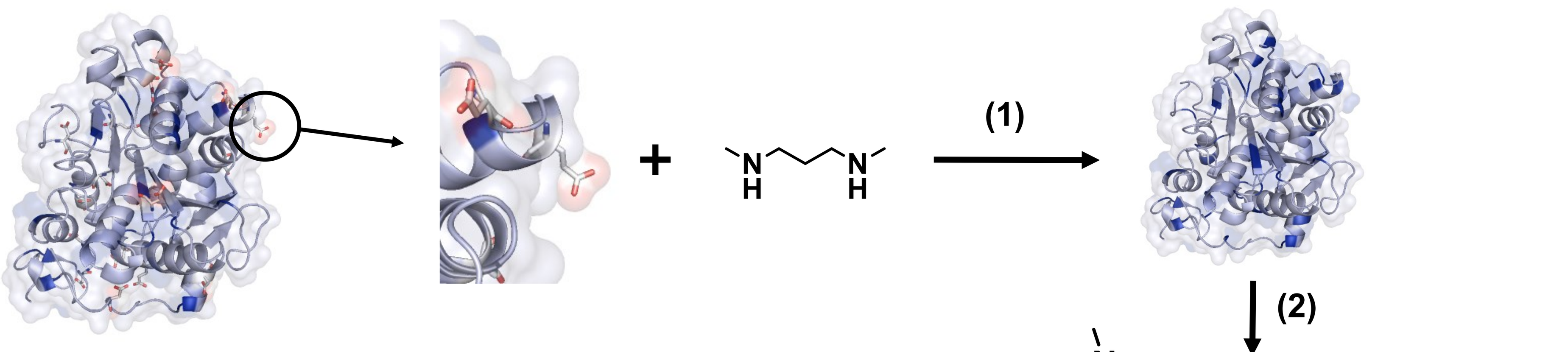
Introduction

Despite the clear hazard to living systems caused by **accumulation of plastic** in the environment, less than 50% of plastic waste is currently recycled in the UK, with the rest sent to landfills or incinerated.[1] One possible solution to generate a more **sustainable circular economy** is presented through the use of enzymes to break down plastics to monomers.

Brogant *et al.* have previously demonstrated that proteins can be **chemically modified** to form biofluids with an improved **thermal stability** and **enzymatic activity** in different ionic liquids.[2-4]

Here, we show the advantages acquired from mixing chemically modified Lipase B from *Candida antarctica*, **CalB**, and **ionic liquids** for the degradation of poly(lactic acid), **PLA**.

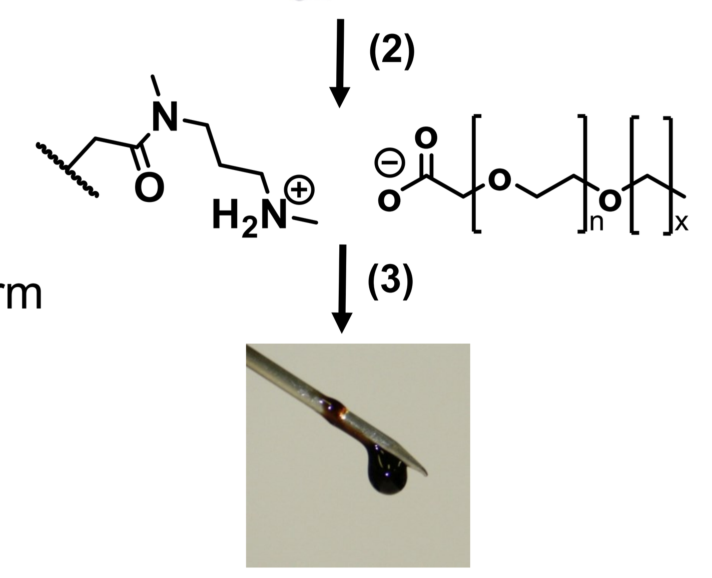
Protein modifications



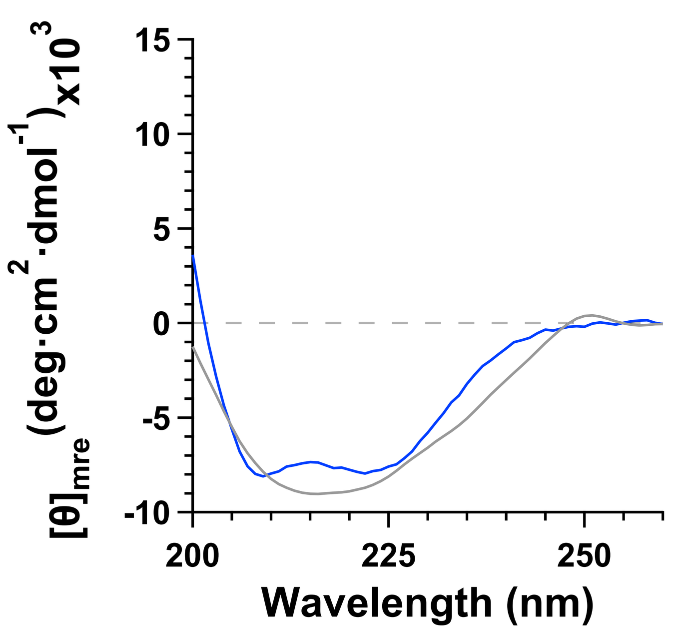
(1) **Cationization** of surface carboxylic acid residues (Asp and Glu) of CalB.

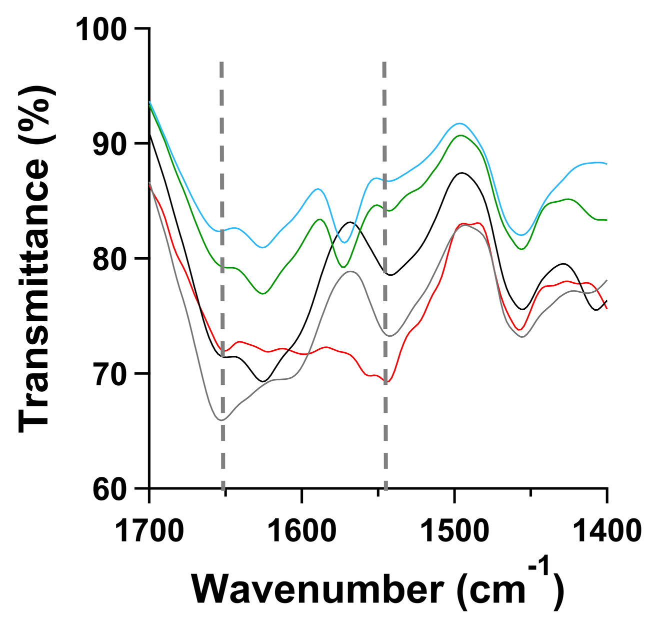
(2) **Electrostatic coupling** of polymer surfactant to form the nanoconjugated CalB, [C-CalB][S].

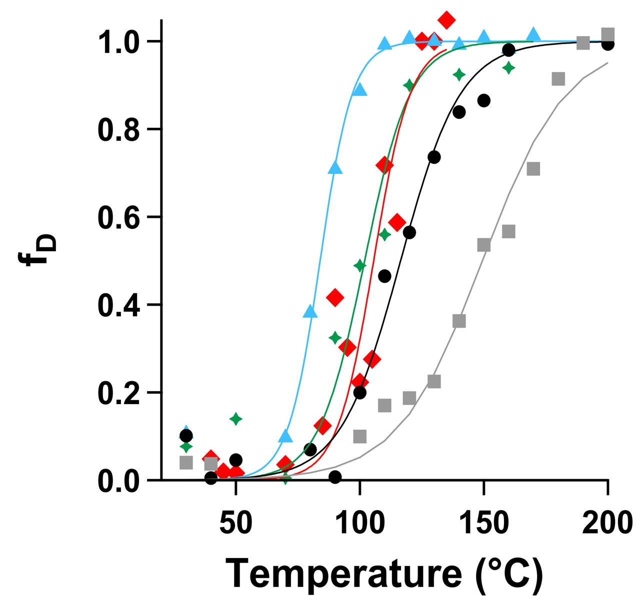
(3) **Lyophilisation** and **annealing** of nanoconjugated CalB to yield **solvent-free liquid protein**.



Stability of modified lipase in anhydrous solutions

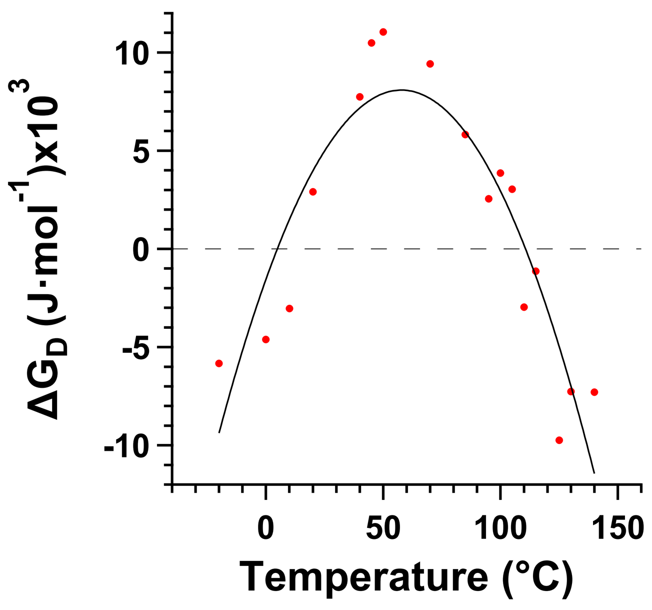


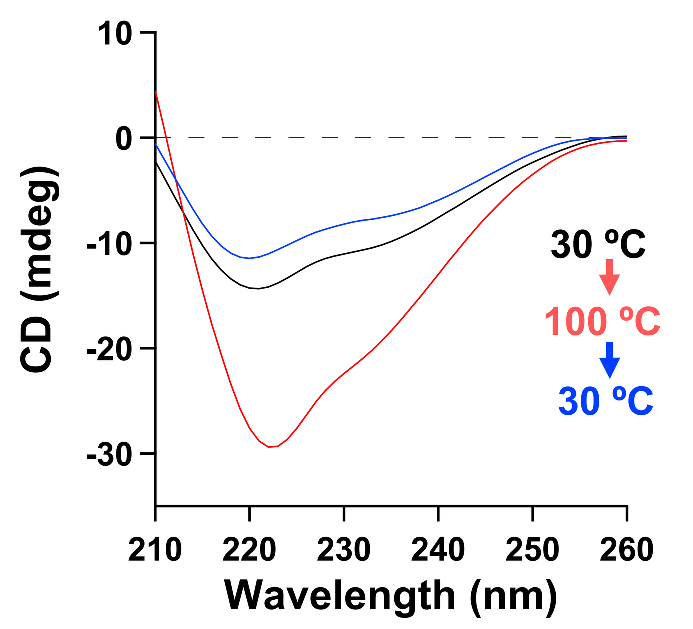


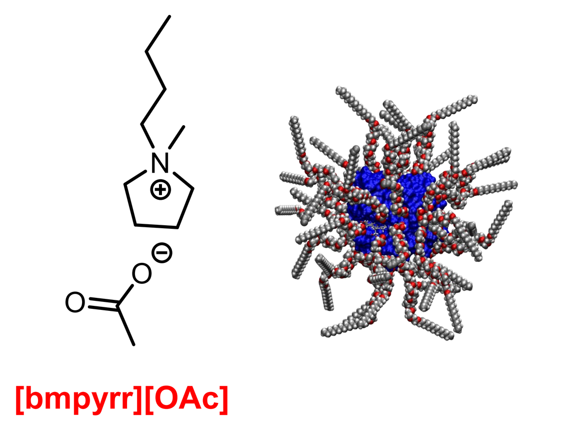


- High conservation of secondary structure (SCRD) in the absence of water.
- Secondary structure is retained in ionic liquids as predominately α-helix (FTIR).
- Higher thermostability in anhydrous conditions (T_m > 80 °C) than in water (T_m = 71 °C)

Key: Aqueous
Solvent-free biofluid
[bmpyrr][OAc]
[bmpyrr][MeSO$_4$]
[bmpyrr][OTf]
[bmpyrr][NTf$_2$]



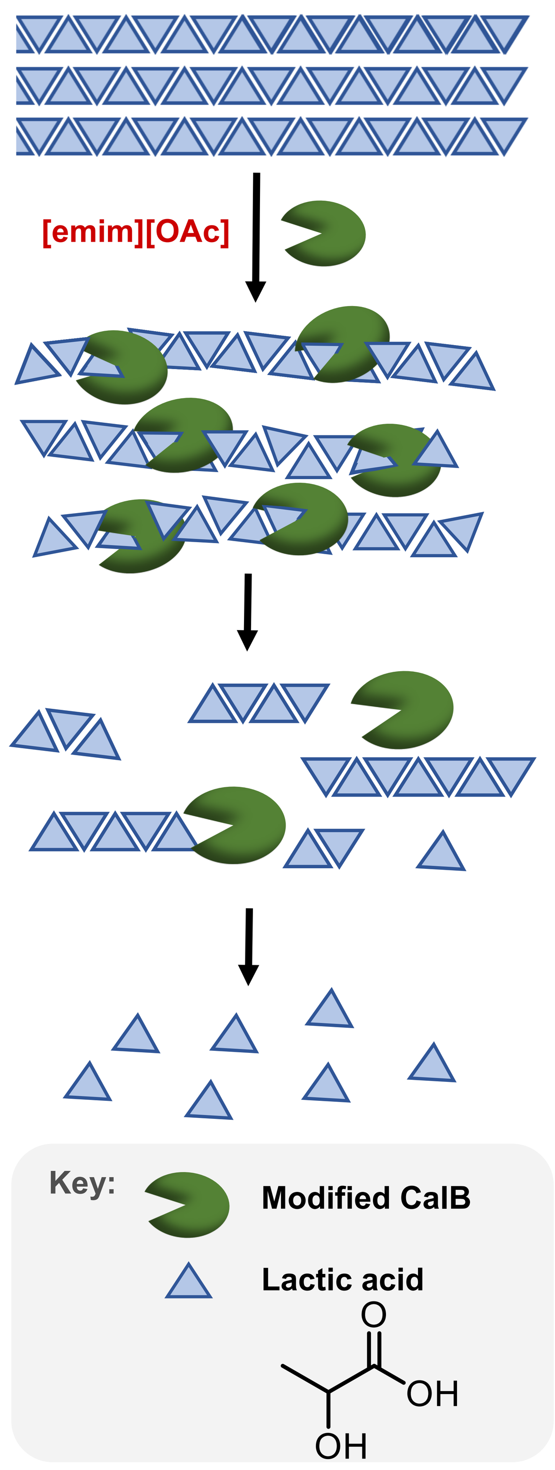


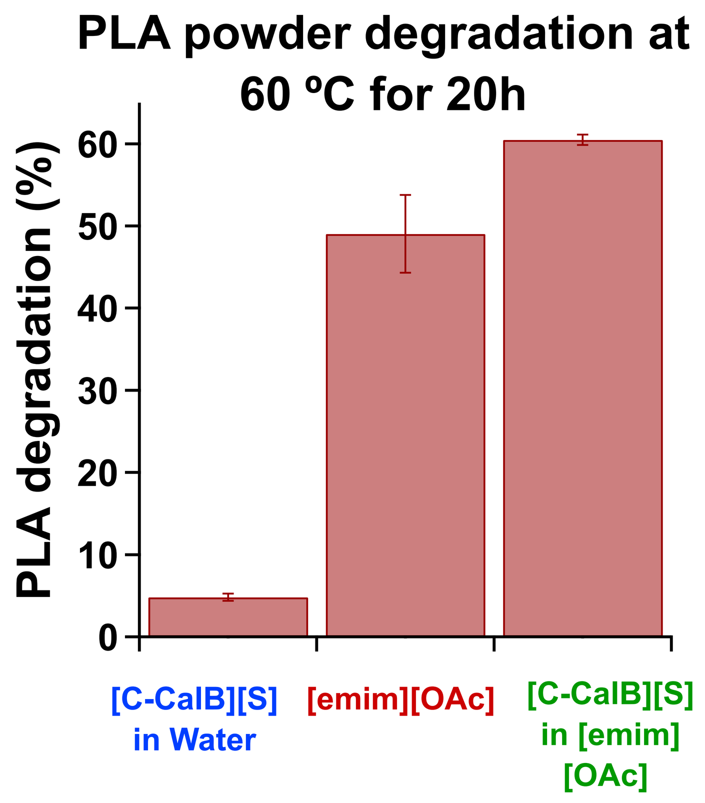


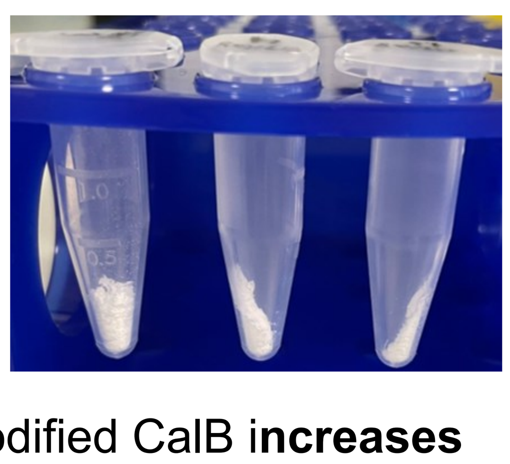
Modified CalB in [emim][OAc] forms:

- A **thermophilic material** with high structure stability between 30 and 90 °C.
- A **dynamic material** able to almost fully recover its structure after heating.

Modified lipase in [emim][OAc] for the degradation of PLA

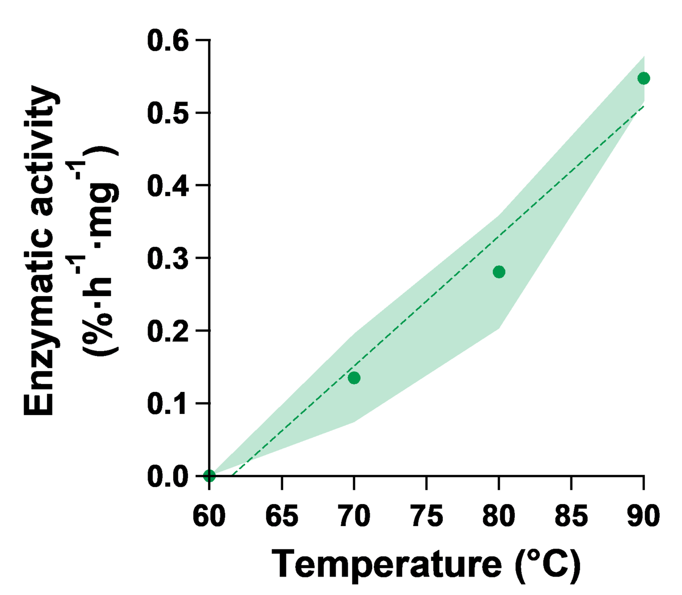


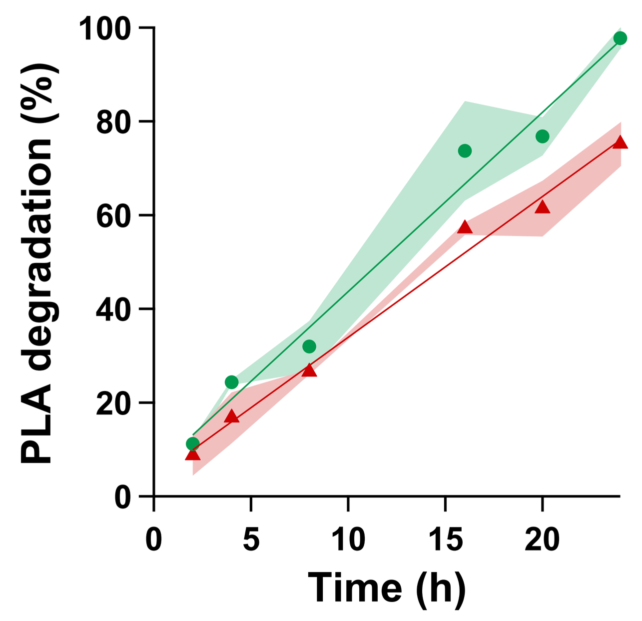


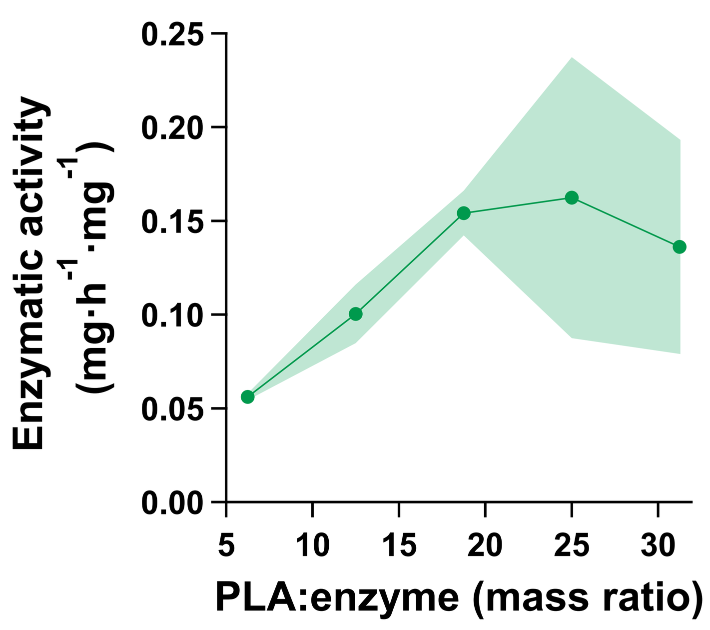


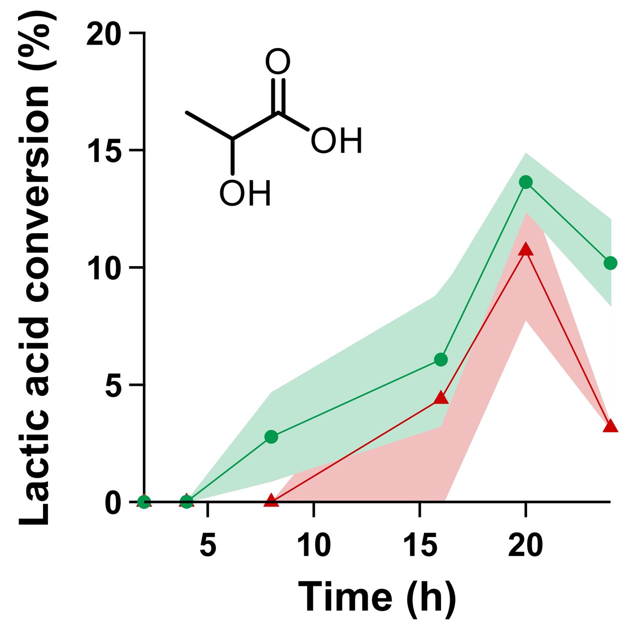
- Modified CalB **increases 11%** the degradation of PLA powder.

Post-consumer PLA plastic degradation

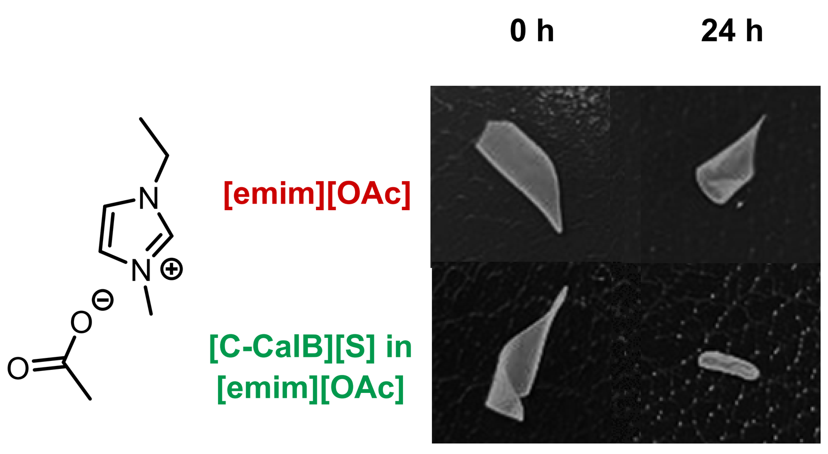








Key: [C-CalB][S] in [emim][OAc]
[emim][OAc]



Activity of the modified CalB for the degradation of PLA plastic in [emim][OAc]:

- Activity **increases with increasing temperature.**
- **zero-order kinetics** - modified CalB is not inhibited.
- The **maximum activity** of modified CalB is 0.15 mg·h⁻¹·mg⁻¹.
- Modified CalB improves **lactic acid production.**

Conclusion

CalB was successfully stabilised by chemical modifications, showing a preservation of its secondary structure in anhydrous conditions with a high α-helix content, and a high thermal stability in ionic liquids. Furthermore, solubilising modified CalB in [bmpyrr][OAc] resulted in a dynamic and thermally stable material able to degrade post-consumer PLA plastics at 90 °C.

As a result, we showed that chemical modification can improve protein stability. Moreover, through combining modified enzymes and ionic liquids, we can improve their enzymatic activity to degrade long plastic polymers.

References

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