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Enzymatic depolymerization of polylactide into repolymerizable monomers using sustainable conditions.

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PURPOSE OF THE ABSTRACT

Bioplastics are often seen as a solution to answer the problems associated to petro-sourced plastics. One of the most famous is polylactide, also known as PLA, representing 24% of the global production of bio-based plastics (1). This is a bioplastic made from lactic acid (L-lactic acid mainly), produced by fermentation of renewable resources (e.g. corn, potato...) and is mainly produced by polymerization of L-lactide (i.e. cyclic dimer of L-lactic acid) by Ring Opening Polymerization (ROP). In addition to its bio-sourced nature, PLA has the advantage of having similar characteristics to some conventional plastics such as polystyrene (PS) or polyethylene terephthalate (PET) (2). Even if PLA is a bio-based thermoplastic, it can be at the origin of the same environmental pollution as conventional plastics, considering that it degrades hardly and slowly in nature. Moreover, the European Commission has stated its ambition to reach 100% recyclable packaging on the European market by 2030. Consequently, PLA recycling processes must be put in place to meet these different challenges.

Concerning recycling of plastics, it is distinguished mainly two methods: mechanical recycling and chemical recycling. This work explored the way of chemical recycling of poly(L-lactic acid), by depolymerizing it into directly repolymerizable monomers (i.e. lactide/cyclic oligomers vs. lactic acid), which will be reused in the same (closed-loop) application enabling “infinite recycling” (3). It exists different ways to break down the PLA chains among which hydrolysis, alcoholysis and pyrolysis are highly studied in academic fields. Pyrolysis, based on the use of high temperatures (> 600 °C) makes the degradation of the polymer into easily repolymerizable products (e.g. cyclic oligomer, lactide...). However, this strategy is hard to implement at industrial scale and it causes side reactions (e.g. epimerization, acrylic acid generation...) (4). In order to use a lower temperature, from which the thermodynamic equilibrium is shifted towards the depolymerization side (known as ceiling temperature or Tc) and which limits the secondary reactions, solvents can be used (5). This strategy enables the recovery of useful repolymerizable cyclic oligomers and is often described as Ring Closing Polymerization (RCP) or cyclodepolymerization (CDP), which constitutes the opposite reaction of ROP (6). Cederholm et al. obtained high yields of lactide (> 95%) after short times (1-4h) using Sn(Oct)2 as a catalyst and different solvents (7). Takahashi et al achieved to produce cyclic oligomers via enzymatic depolymerization of PLLA into o-xylene (8). The present work aims to use renewable and sustainable biocatalyst (Novozyme 435®, an immobilized Lipase B from Candida antarctica) and green solvents (Dimethyl carbonate (DMC) and diethyl carbonate (DEC)) to enable the recovery of repolymerizable cyclic oligomers of lactid acid from PLA with various degrees of crystallinity. First, DMC and DEC have demonstrated a good ability to solubilize PLA reaching final concentrations of 120 g.L-1 in both solvents using a PLA with high crystallinity degree (χc = 49.66 ± 7,21 %) and high temperatures. Moreover, it has been demonstrated that Novozyme 435® (N435®) still maintains activity after different times (from 2 to 48 hours) at high temperatures (from 80 to 120 °C) in both solvents, making it suitable for the depolymerization of PLA at high temperature in solvent media. DMC and DEC, being organic carbonate solvents, their reactivity in presence of

N435® at high temperatures have also been explored by Gas Chromatography (GC) analysis in order to check their stability. Finally, Size Exclusion Chromatography (SEC) analysis have been set up to evaluate the decrease in molar mass of the polymer. Future objectives will be to analyze low-weight oligomers produced (e.g. using 1H NMR) and investigate their repolymerizability by N435® in sustainable conditions.

FIGURES

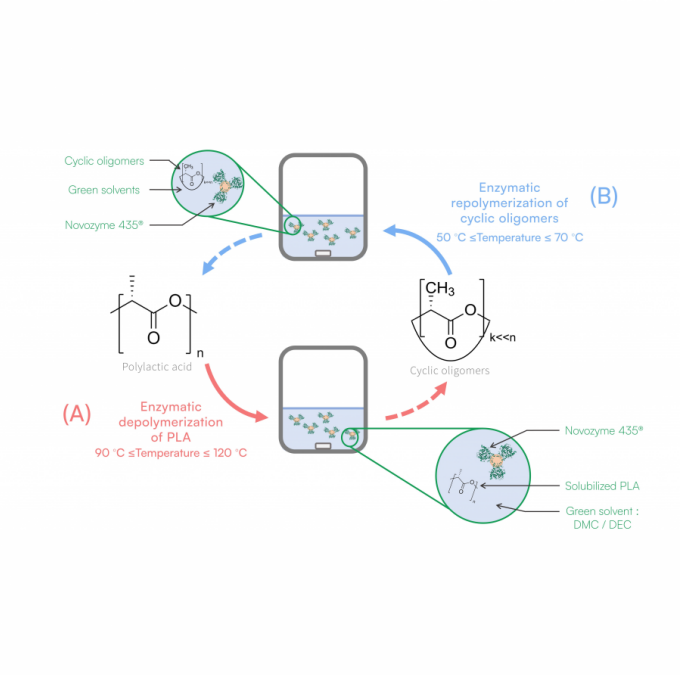

FIGURE 1

Representative schema of the enzymatic depolymerization of PLA into repolymerizable products and their enzymatic repolymerization

(A) : Enzymatic depolymerization of PLA solubilized in green solvents (e.g. dimethyl carbonate or diethyl carbonate).

(B) : Enzymatic repolymerization of oligomers in green solvents

FIGURE 2

KEYWORDS

Polylactide | Cyclo Depolymerization | Novozyme 435 | Green solvent

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