Preparation and characterization of bio-based co-polyesters: interest and limitations

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Background

- The global fossil-fuel economy has jeopardized the planet's resources and resilience, resulting in climate change.
- The European Commission emphasizes the need for alternative sustainable plastics to meet rising demand [1], and bio-based polymers are a current research hot subject.
- Polyesters have tunable characteristics, a broad application range, and great recyclability[2].

Objectives

- Synthesize co-polyester from bio-based monomers (diacid/s + diol) extracted from non food and feed resources.
- Study the effect of monomer compositions on polymer properties.
- Aim for a greener and cleaner polymerization.
- Justify the results with LCA studies

Key acronyms

- SA: sebacic acid
- FDCA: 2,5-furandicarboxylic acid
- FDME: furan dicarboxylic methyl ester
- DES: diethyl sebacate
- BDO: 1,4-butanediol
- ODO: 1,8-octanediol
- DPE: diphenyl ether
- TBT: tetrabutyl titanate
- CALB: *Candida antarctica* lipase B
- MeOH: methanol
- $CHCl_3$: chloroform

Methodology

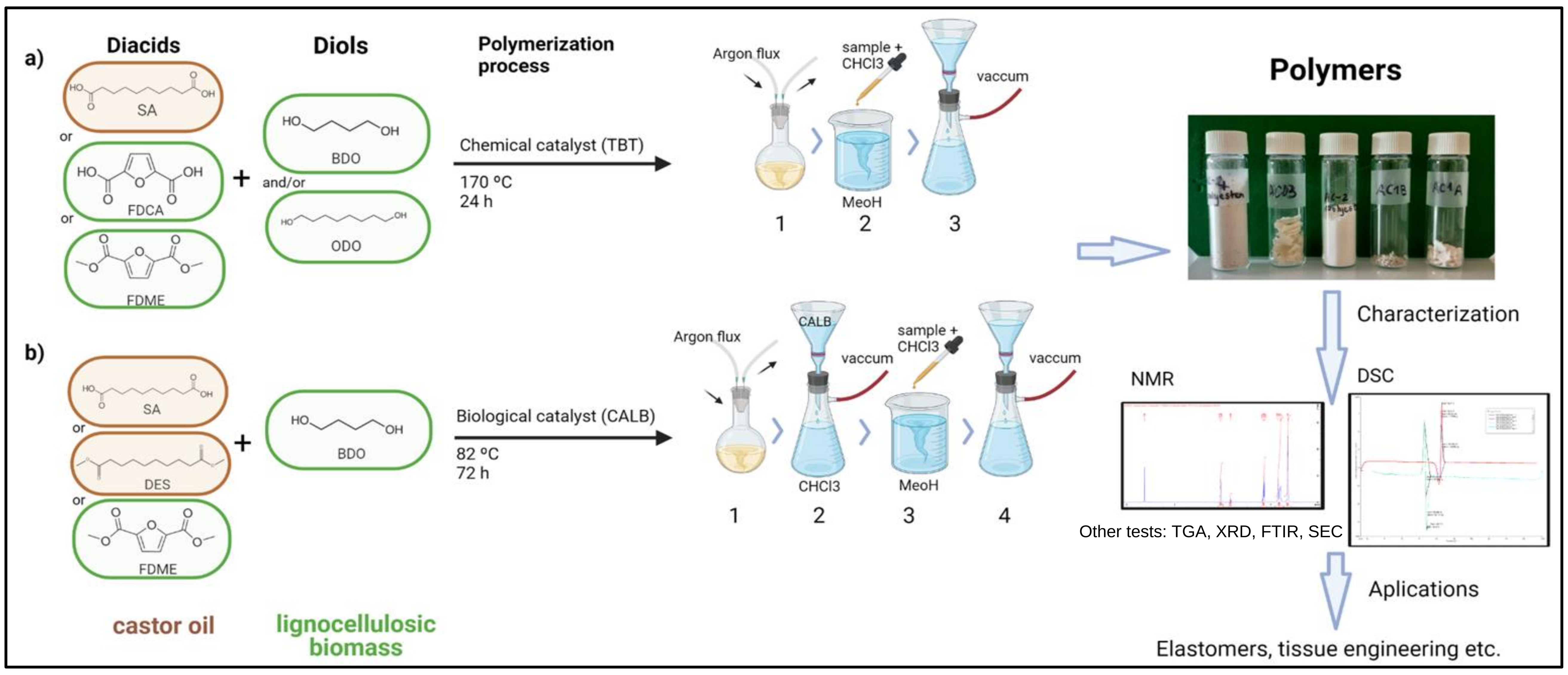
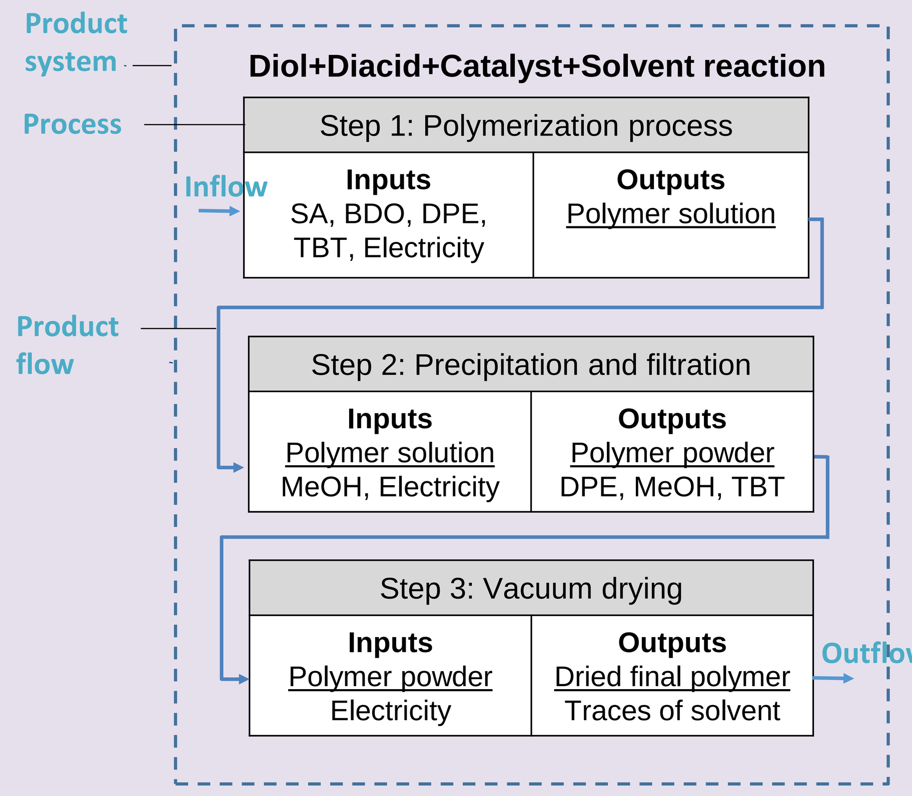


Figure 2: Stepwise procedure to synthesize co-polyester

Life Cycle Analysis



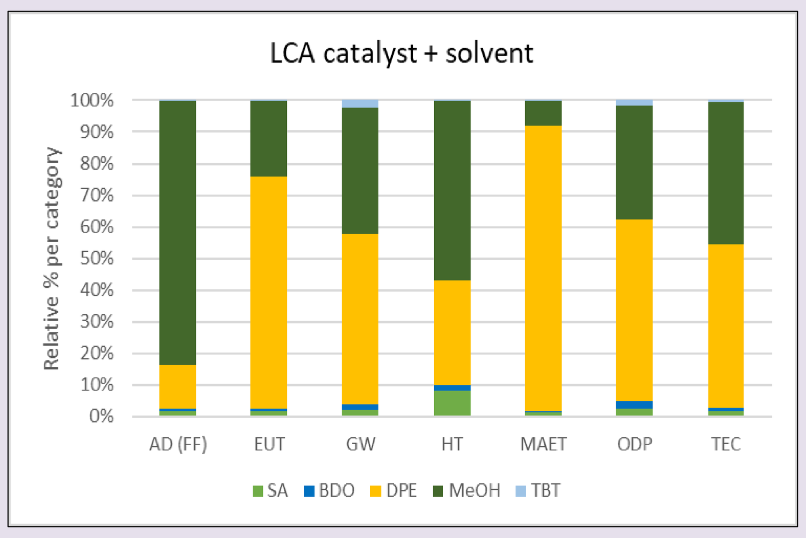


Figure 1: Bar graph of LCA impact categories for reactants in the polymerization.
Impact categories- AD (FF) abiotic depletion (fossil fuels); EUT: eutrophication; GW: global warming; HT: human toxicology; MAET: marine aquatic ecotoxicology; ODP: ozone layer depletion; TEC: terrestrial ecotoxicology.

- DPE solvent - key contributor in all the impact categories.
- TBT catalyst - 2nd key contributor in ODP and GW.
- No solvent, no catalyst- good for environment

Results and Discussions

A. Proof of Polymerization

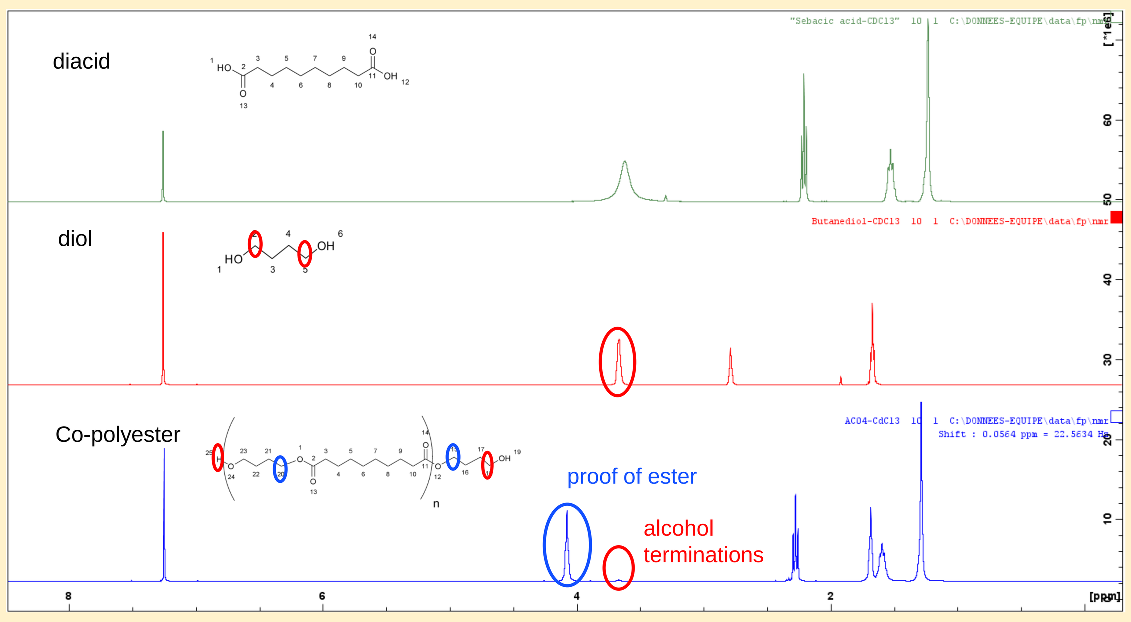


Figure 3: ¹H NMR spectrum of the co-polyester synthesised in comparison to the spectrum of the monomers, SA (diacid) and BDO (diol).

🔵 H attached to carbonyl groups and the corresponding peak on the spectrum.

🔴 H attached to carbon with the alcohol terminating group.

Reactants: SA+ BDO

- **Proof of ester bond:** Peak at 4.1 ppm [3,4]

B. Impact of ratio of mixture of 2 different diols on polyesterification

Number	BDO (mole%)	ODO (mole%)	Melting point (°C)	Yield (%)	Polymer aspect
1	0	100	67.4	90.4	White powder
2	25	75	59.5, 65.7	117 (traces of solvent)	White powder
3	50	50	62.0	109 (traces of solvent)	Off white flocs
4	75	25	51.0, 54.6	74.4	Off white flakes
5	100	0	65.1	75.3	White powder

Table 1: Results from DSC compared with yield and aspect of the co-polyester.

All reactions were performed by chemical catalysis at 170 ºC under argon flux, for 24 h.

Reactants: SA + BDO/ODO

- BDO/ODO (0/100),(100/0) ➡ **single, sharp peak**
- BDO mole%↑ + ODO mole%↓ ➡ **two broad peaks**

C. Catalyst and/or solvent effect on co-polyester properties: aiming for a greener and cleaner reaction

Number	Solvent	Catalyst	Reaction time (h)	Polymer aspect	Polymerization degree*	Melting point (ºC)	Yield (%)
1	Diphenyl ether	TBT	24	White powder	40.7	65.1	75.26
2	Methyl ethyl ketone	CALB	72	White flakes	9.6	55.0	22.04
3	-	TBT	4	White powder	69.5	66.2	8.12
4	Diphenyl ether	-	24	Yellowish powder	17.9	56.4	64.47
5	-	-	24	Yellowish powder	39	54.4	72.07

Table 2: Results from DSC compared with yield, polymerization degree and aspect of the co-polyester.

Reactants: SA + BDO

- No solvent, no catalyst co-polyester synthesis is possible [5].
- **Chemical catalyst** aids **long chain co-polyesters** compared to biocatalyst.
- **No solvent and no catalyst** give **same length co-polyesters** as with **chemical catalyst and solvent.**
- Co-polyester synthesized without catalyst = high polydispersity.
- No solvent, no catalyst = cleaner, metal free reactions (biomedical applications [6]).

Conclusions and Perspectives

- Co-polyester without solvent and catalyst is demonstrated. Further studies to study the co-polyester characteristics is to be carried out further.
- Despite the non-competitive market pricing of the bio-based polyesters, better properties and niche application probabilities make them viable and interesting. Maturation of the biorefinery model to reduce monomers costs is key for this technology to scale up.

Scan for references