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.
• Polymers 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.

Methodology

Key acronyms
- SA: sebacic acid
- FDCA: 2,5-furandicarboxylic acid
- FDME: furan dicarboxylic methyl ester
- DES: diethyl sebacate
- BDO: 1,4-butandiol
- ODO: 1,8-octandiol
- DPE: diphenyl ether
- TBT: tetraetyl titanate
- CALB: Candida antarctica lipase B
- MeOH: methanol
- CHCl₃: chloroform

Results and Discussions

A. Proof of Polymerization

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

<table>
<thead>
<tr>
<th>Num ber</th>
<th>BDO (mole%)</th>
<th>ODO (mole%)</th>
<th>Melting point (ºC)</th>
<th>Yield (%)</th>
<th>Polymer aspect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>100</td>
<td>67.4</td>
<td>90.4</td>
<td>White powder</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>75</td>
<td>59.5, 65.7</td>
<td>117 (sharp of solid)</td>
<td>White powder</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>50</td>
<td>62.0</td>
<td>109 (sharp of solid)</td>
<td>Oil white flakes</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>25</td>
<td>51.0, 54.6</td>
<td>74.4</td>
<td>Oil white flakes</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>0</td>
<td>65.1</td>
<td>75.3</td>
<td>White powder</td>
</tr>
</tbody>
</table>

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

Reagents: SA + BDO
- Proof of ester bond: Peak at 4.1 ppm [3,4]

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.

Figure 2: Stepwise procedure to synthesize co-polyester

Figure 3: ¹H NMR spectrum of the co-polyester synthesized 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

Figure 1: Bar graph of LCA impact categories for reactants in the polymerization.

Impact categories: AD (FP) abiotic depletion (fossil fuels); EUT: eutrophication; GW: global warming; H7: human toxicity; 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