

Recyclable Thermosetting Materials from Renewable Sources: Synthesis and Characterization of PLA-Based Thermosets

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INTRODUCTION

The increasing amount of plastic waste derived from fossil fuels contaminating our environment is one of the most critical issues of our time.^[1] While thermoplastics are relatively easy to recycle, thermosets are challenging due to their stable cross-links.

However, thermosets have superior properties, making them useful in various fields, which necessitates their inclusion in a circular economy. "Covalent adaptable networks" (CANs) or "vitrimers" offer a solution, as they behave like traditional thermosets but can be reprocessed and chemically recycled due to their weaker cross-links. Additionally, the starting monomers used for the synthesis of these polymers can be obtained from renewable sources.^[2]

Thermoplastic

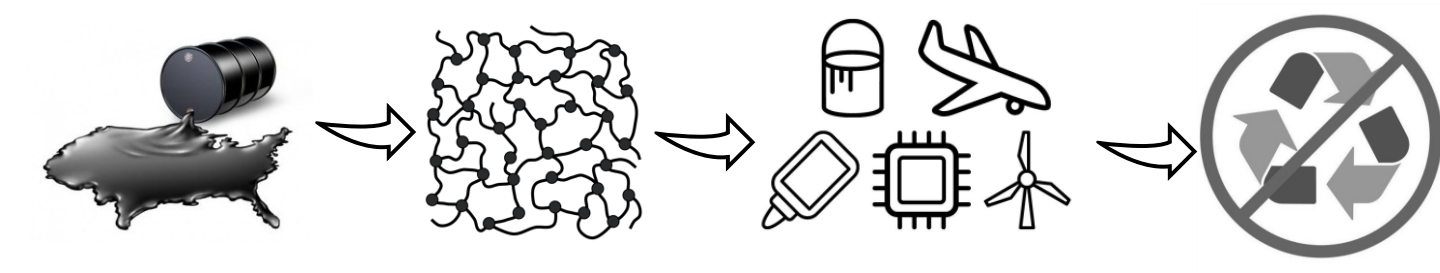


Vs



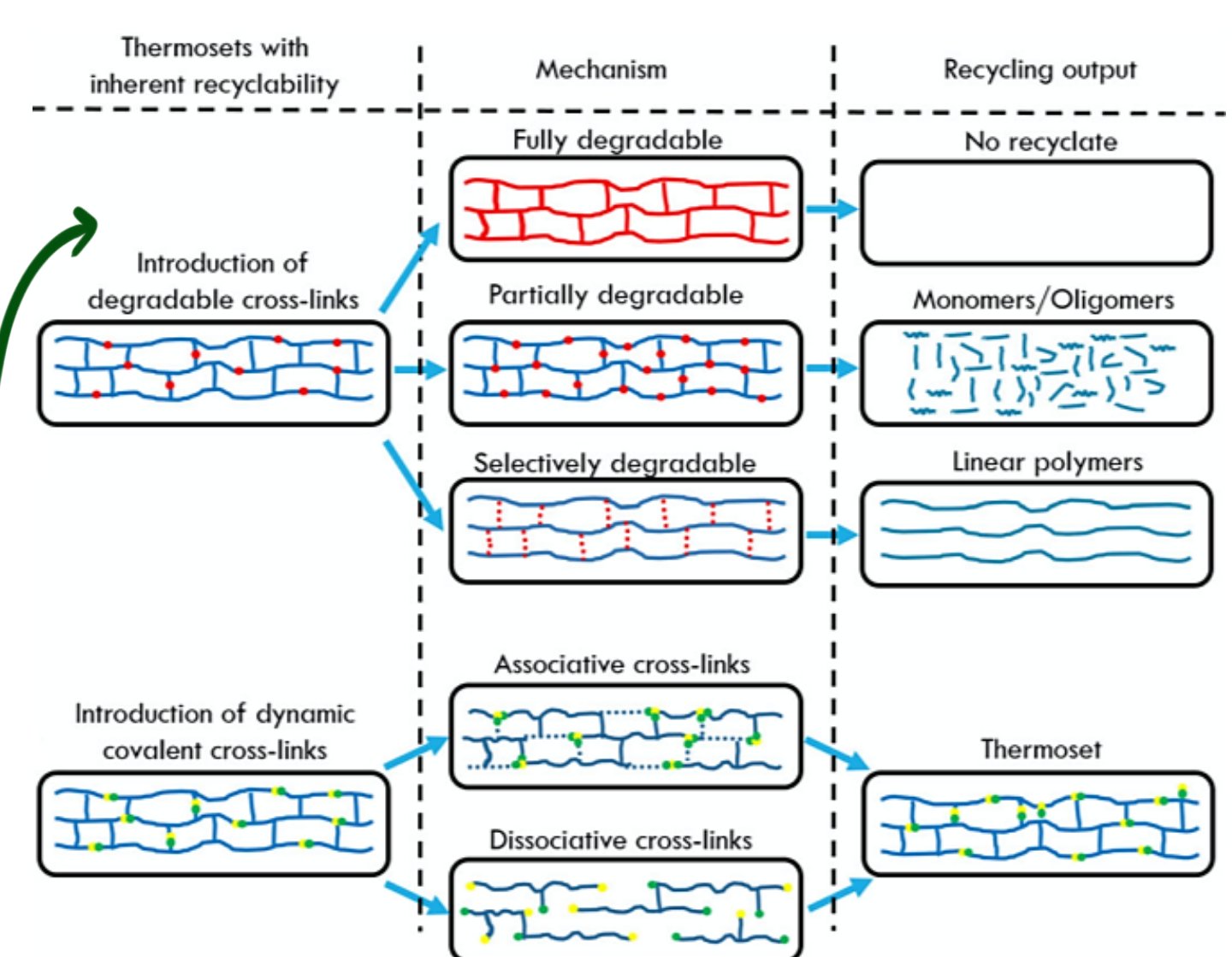
Thermoset

Thermoset linear life



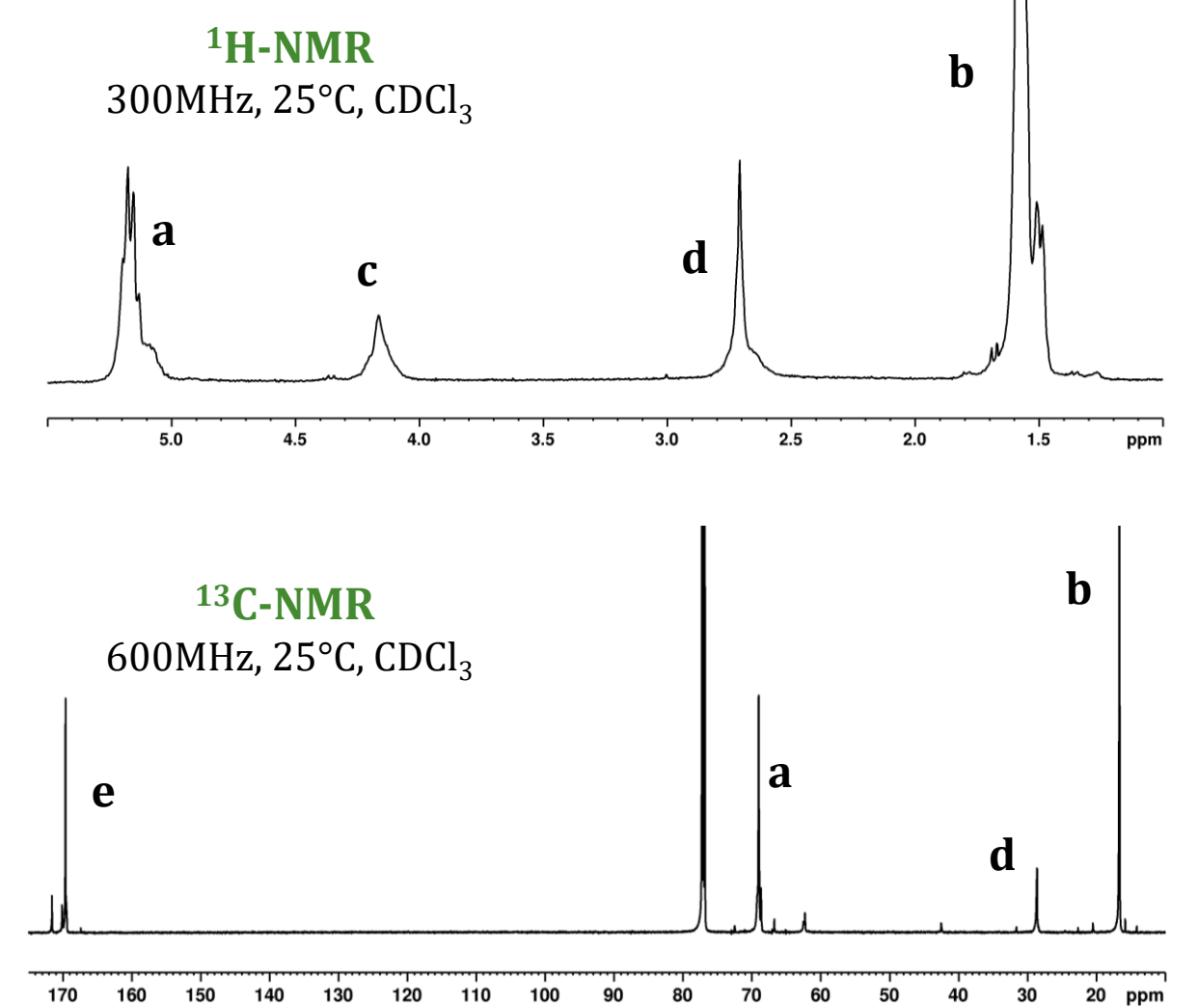
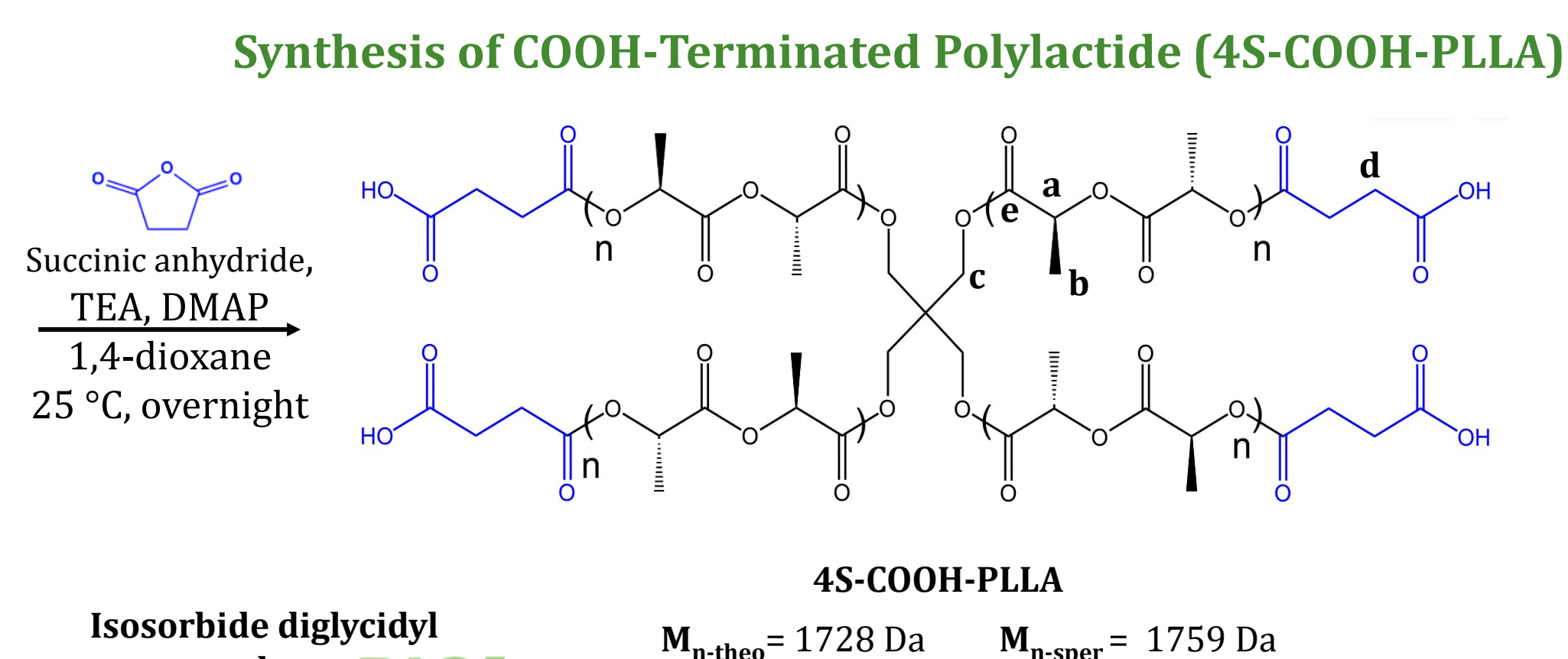
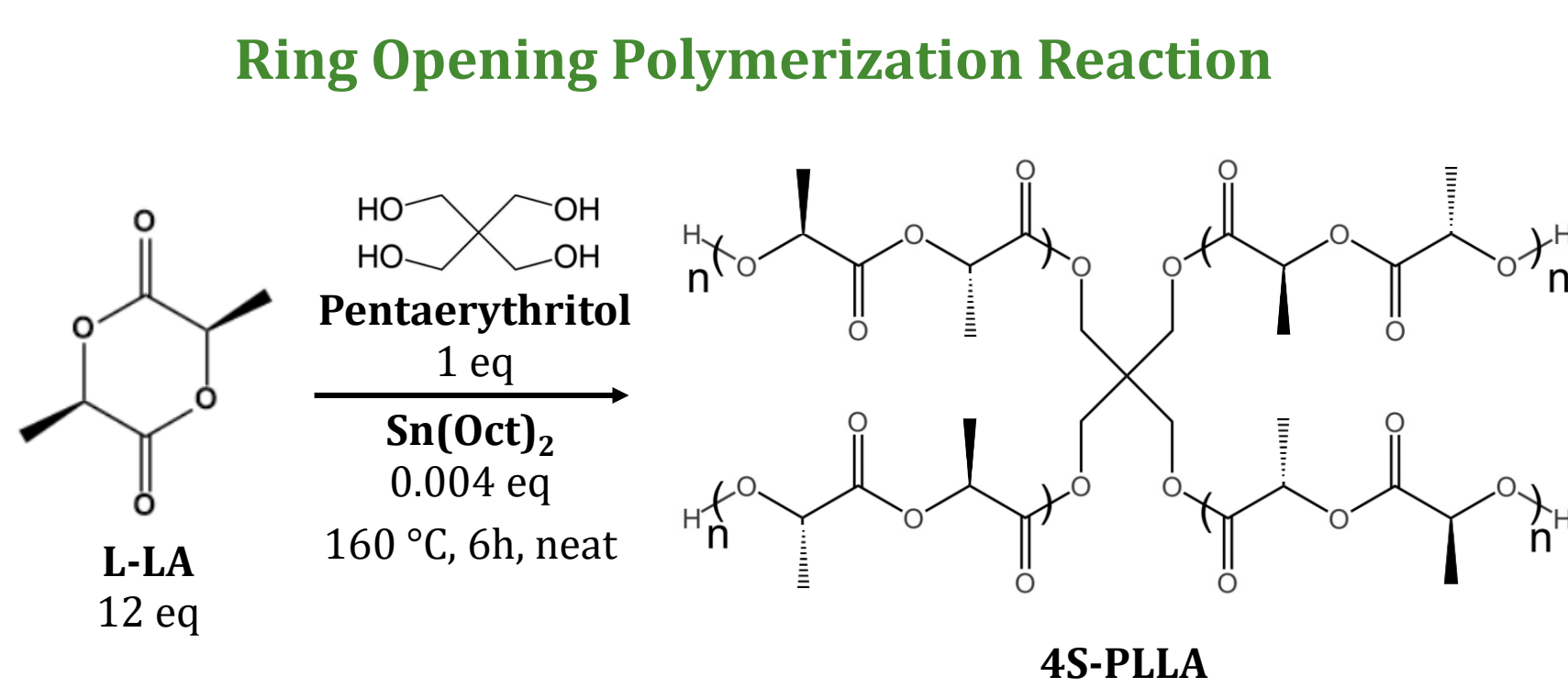
New proposed approach

Property	Thermoplastics	Thermosets
Molecular Structure	Composed of linear polymers with weak bonds	Composed of network polymers with strong bonds
Melting Point	Melting point lower than degradation temperature	Melting point higher than degradation temperature
Microstructure	Comprise elastic amorphous and hard crystalline regions	Consist of solid resin and reinforcing fibers
Mechanical	Flexible, elastic and impact resistant; strenght from crystallinity	Brittle and inelastic; strenght from crosslinking
Recyclability	Recyclable and reusable	Not recyclable
Chemical resistance	Highly resistant to chemicals	Resistant to chemicals and heat
Solubility	Can dissolve in organic solvent	Insoluble in organic solvent

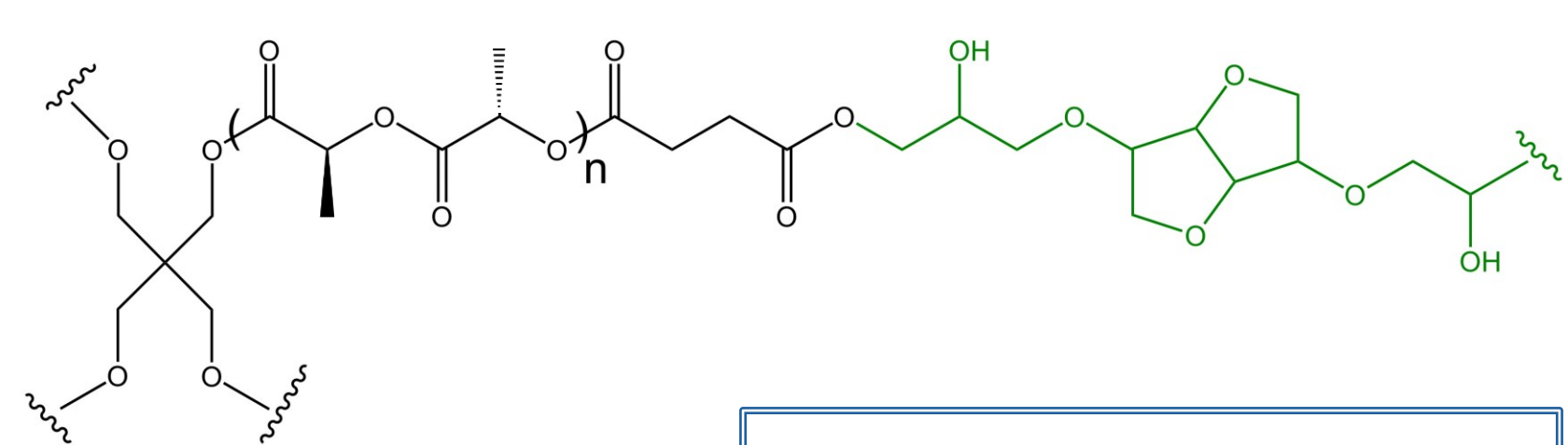
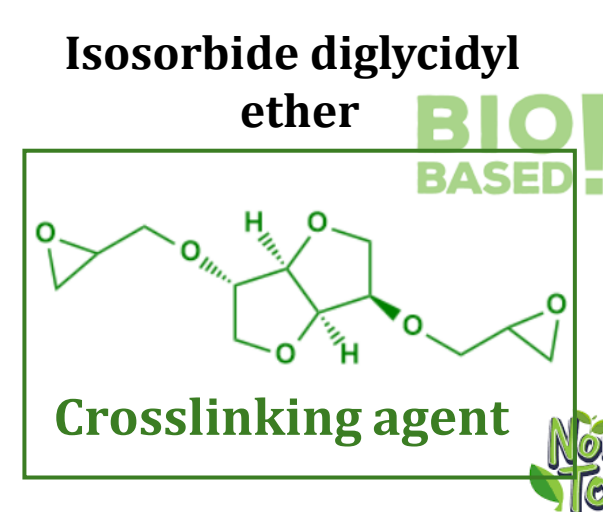
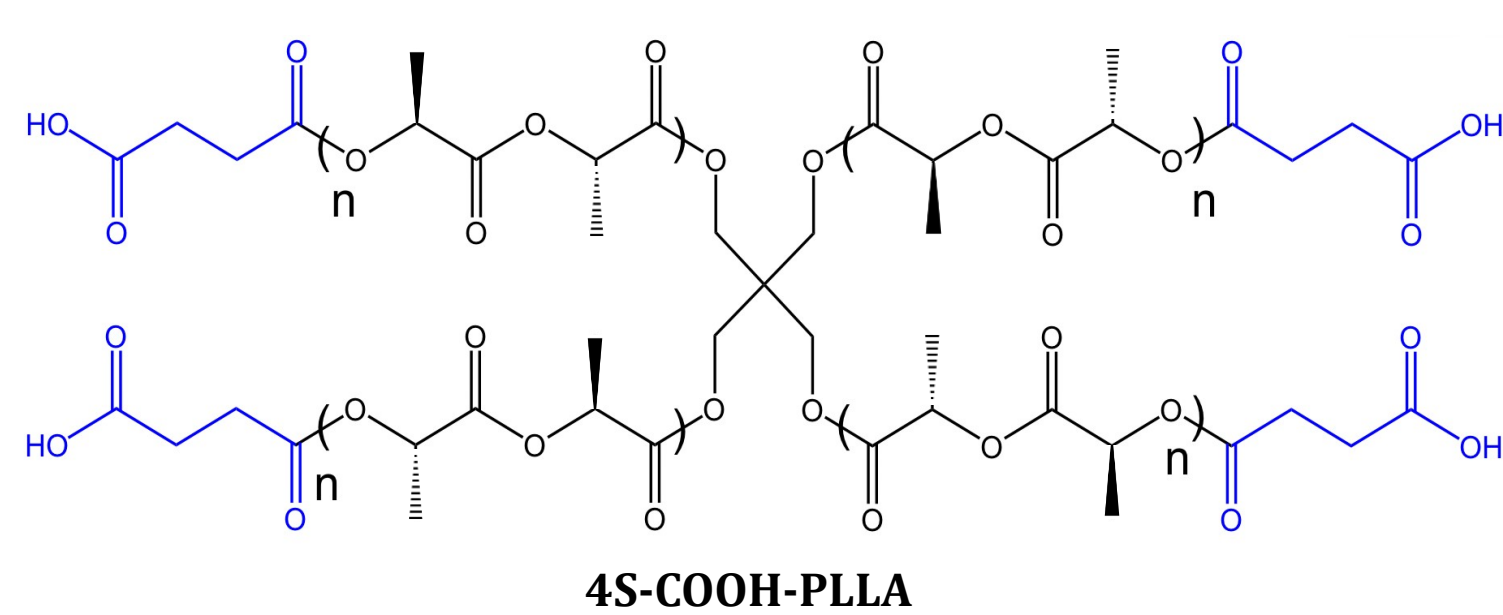


RESULTS AND DISCUSSION

Synthesis of branched pre-polymer obtained from renewable sources



Curing reaction



CONCLUSION

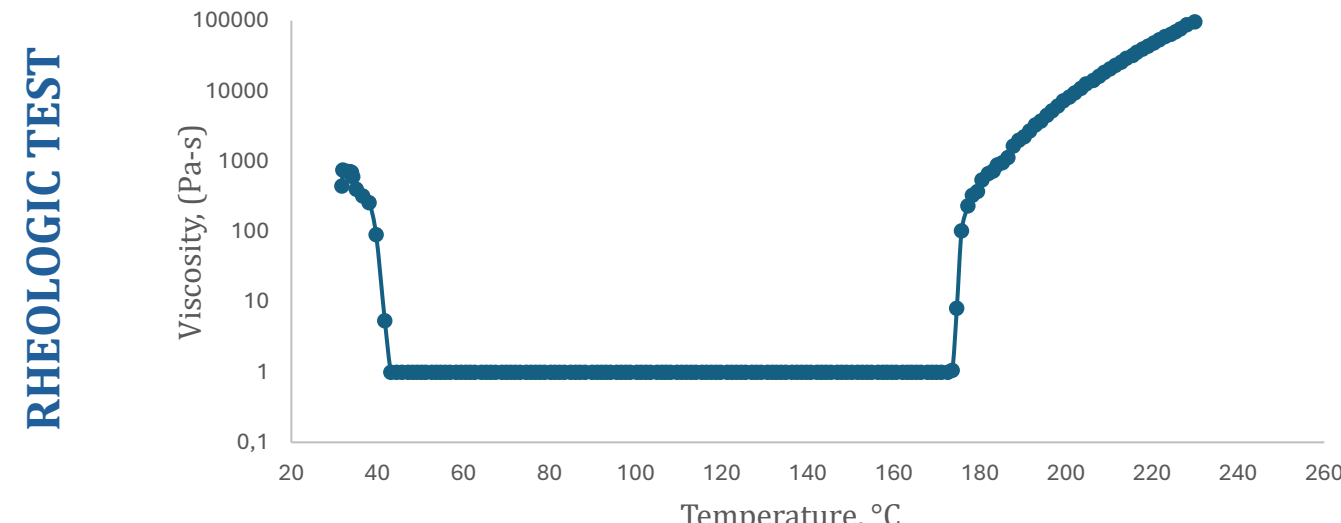
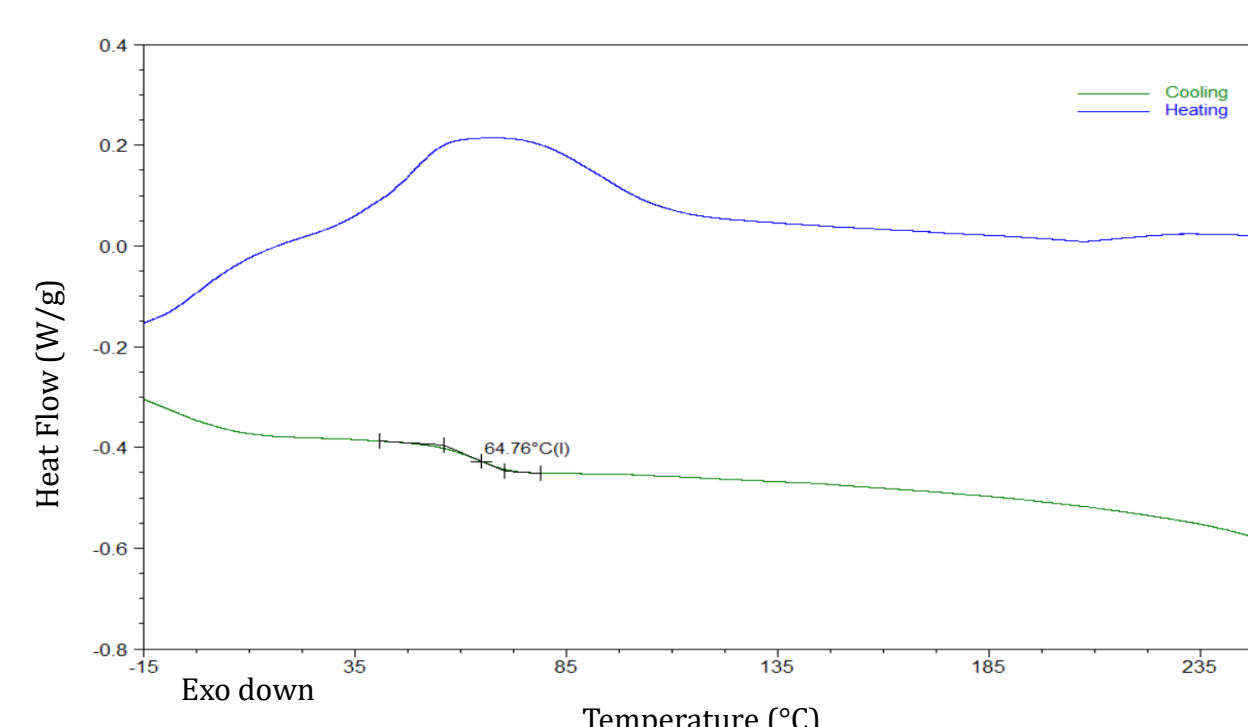
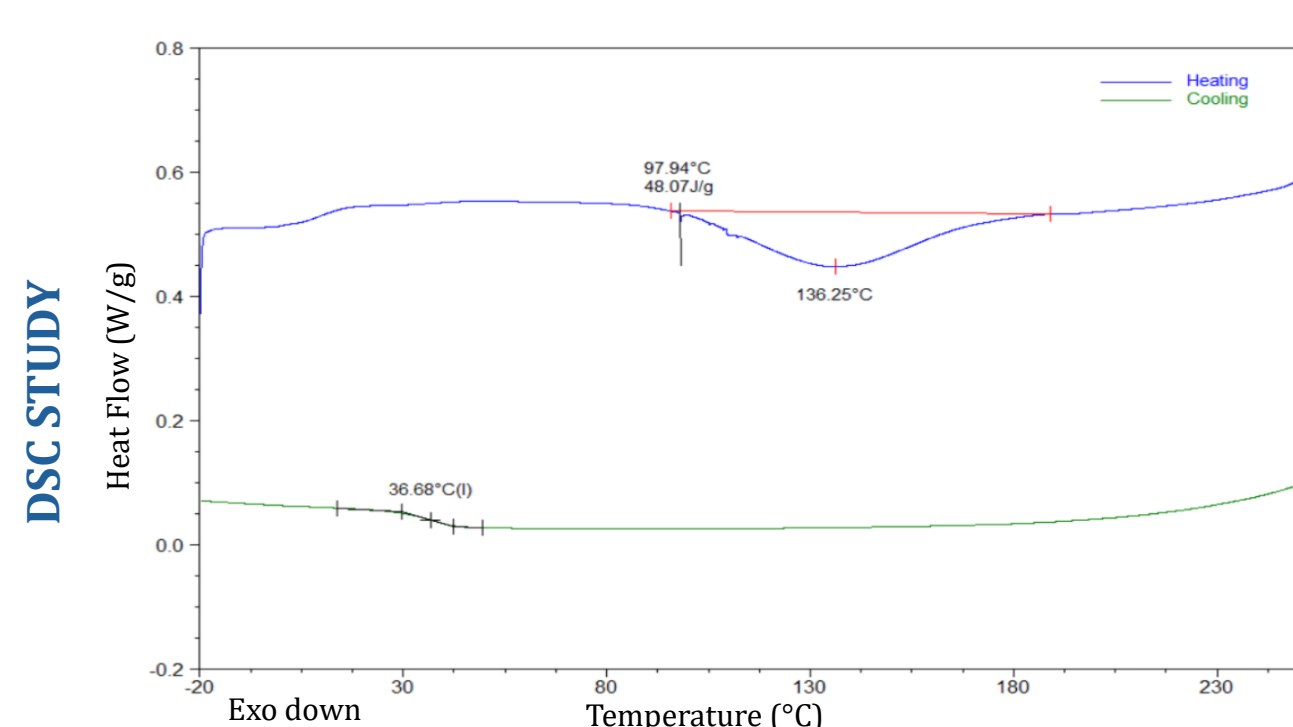
In this work a new completely biobased thermosetting material was synthesized starting from a branched PLA-based prepolymer with star geometry subsequently functionalized by reaction with succinic anhydride. The prepolymers were then crosslinked using isosorbide diglycidyl ether (DGEIs),^[3] a bis epoxide obtainable from sugars like sorbitol, under different curing conditions. From the various tests carried out, it is observed that the best treatment conditions involve the use of a $[fz_{\text{epox}}] : [fz_{\text{COOH}}] = 1:1$ ratio, 10%_{mol} Zn(OAc)₂ in respect to the $[fz_{\text{COOH}}]$, for 3 hours at 180 °C in oven under nitrogen atmosphere. The obtained materials are insoluble with high gel fractions (>90%) and were characterized via DSC and reology wich confirm the formation of the cross-linked product.

References

- Post W, Susa A, Blaauw R, Molenveld K, Knoop R. J., *Polymer reviews*, **2020**,60(2), 359-388.
- Brutman J. P., Delgado P. A., Hillmyer M. A., *ACS Macro letters*, **2014**, 3(7), 607-610.
- Chrysanthos M., Galy J., Pascault J. P., *Polymer*, **2011**, 52(16), 3611-3620.

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$$\text{Gel fraction (\%)} = \frac{\text{weight after extraction}}{\text{weight before extraction}} \times 100$$

Solvent	Gel Fraction
Chloroform (55 °C)	93%
1,2-Dichlorobenzene (120 °C)	96%