Feasibility of Solid-State Polymerization as an alternative route to synthesize fossil- and bio-based vitrimers from commercially available polyesters

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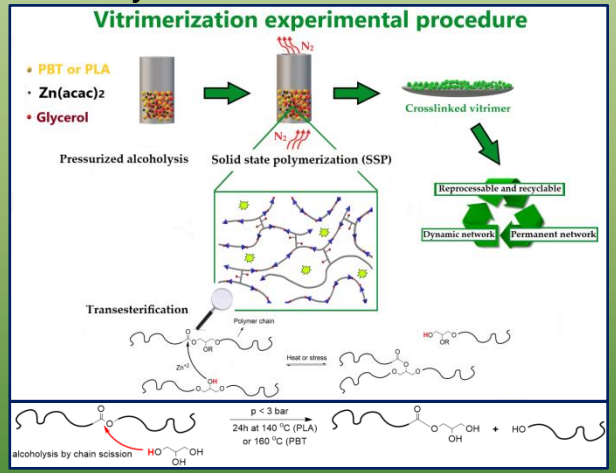
Introduction

Vitrimers, pioneered by Leibler in 2011 **[1]**, constitute a very new class of smart polymeric materials (recyclable thermosets). Topological rearrangement of the dynamic network is thermally stimulated by *associative exchange reactions*, while keeping the number of the bonds and **crosslink density constant**.

Our group holds an extensive research activity on **solid-state polymerization (SSP)** processes **[2].** SSP was herein investigated as an **upscalable tool** for the synthesis of PLA- and PBT-based vitrimers. The **main objective** was to study the influence of the glycerol content on the alcoholysis reactions and establish a correlation between SSP temperature and vitrimers final properties **[3]**.



References

[1] Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-like malleable materials from permanent organic networks. Science **2011**, *334*, 965–968.

[2] Vouyiouka, S.N.; Karakatsani, E.K.; Papaspyrides, C.D. Solid state polymerization. Prog. Polym. Sci. **2005**, *30*, 10–37.

[3] Panagiotopoulos et al. Solid-State Polymerization as a Vitrimerization Tool Starting from Available Thermoplastics: The Effect of Reaction Temperature. Materials **2021**, *14*, 9

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Results

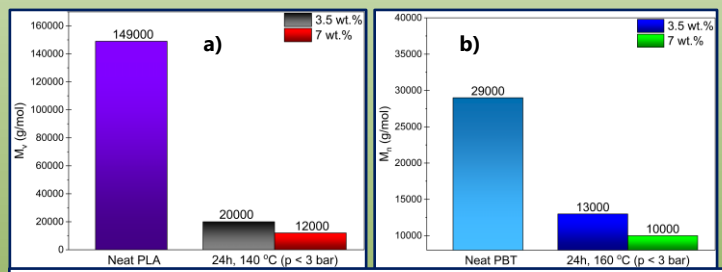

Figure 1. Molecular weight reduction due to alcoholysis reactions with glycerol for **a)** PLA and **b)** PBT

Incorporation of glycerol

Molecular weight reduction by chain scission

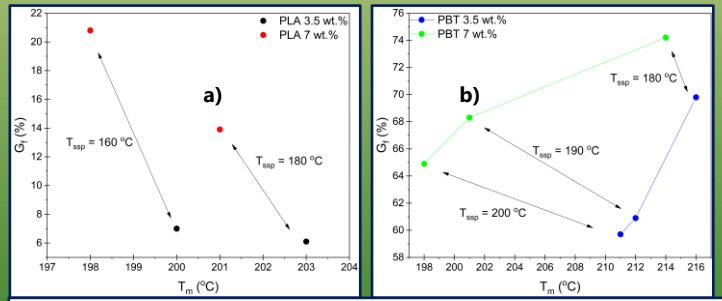

Figure 2. Gel fraction Gf vs. melting point Tm of the produced vitrimers at various SSP temperatures for **a)** PLA and **b)** PBT

Appropriate SSP conditions

160 °C and 180 °C for PLA and PBT vitrimers respectively, in which **maximum Tm and Gf** were observed.

Conclusions

- **Successful** incorporation of glycerol into the polymer chains
- Increased insolubility (especially for PBT) ⟶ **crosslinked structure**
- Tm slightly decreased due to loss of symmetry perfection under the influence of the crosslinks