Vitrimerization of poly(butylene succinate) by reactive melt mixing using Zn(II) epoxy-vitrimer chemistry

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Abstract

Vitrimers constitute a new class of covalent adaptable networks (*CAN*s), in which thermally stimulated associative exchange reactions allow the topological rearrangement of the dynamic network while keeping the number of the bonds and crosslink density constant. In the last years, vitrimers have attracted a great deal of attention due to the combination of **reprocessability** and **improved properties** thanks to the development of a dense crosslinked — yet malleable — structure.

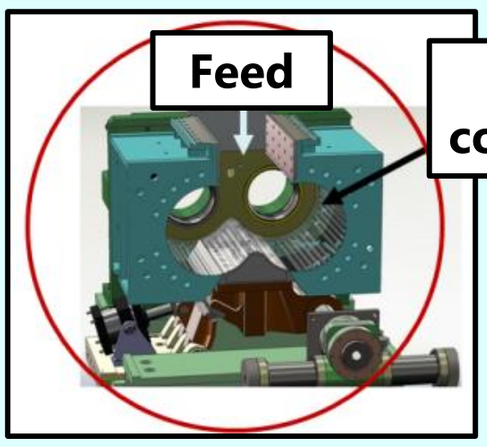
The current study proposed a **solvent-free method** to synthesize vitrimers by a **two-step melt process** using a commercial **biobased and biodegradable polyester, poly(butylene succinate), PBS**. By tuning the crosslinker content (0 – 10 mol % with respect to PBS repeating unit) and thus the Zinc(II) catalyst to crosslinker ratio (0 to 1), tailor-made vitrimers were prepared with high insolubility. PBS vitrimers could still be reprocessed by compression molding after the crosslinking, which enables recycling process.

Methodology

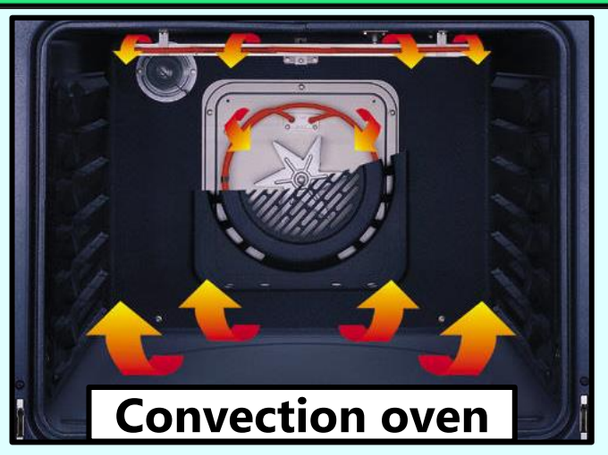
Starting materials

- Commercial extrusion grade PBS (NaturePlast SAS)
- Diglycidyl ether of bisphenol A, DGEBA (SIGMA Life Science)
- $Zn(acac)_2.2H_2O$, Zinc catalyst (Sigma-Aldrich)
- Commercial primary and secondary antioxidants

Melt mixing



Vitrimerization



Results

Insolubility and swelling tests

- Gel fraction increased with DGEBA content and time, while swelling ratio decreased significantly.
- For $PDZ_{10\%}$ gel fraction reached up to 86.1 ± 1.5 % and swelling ratio kept low at 13.9 ± 1.9 %.

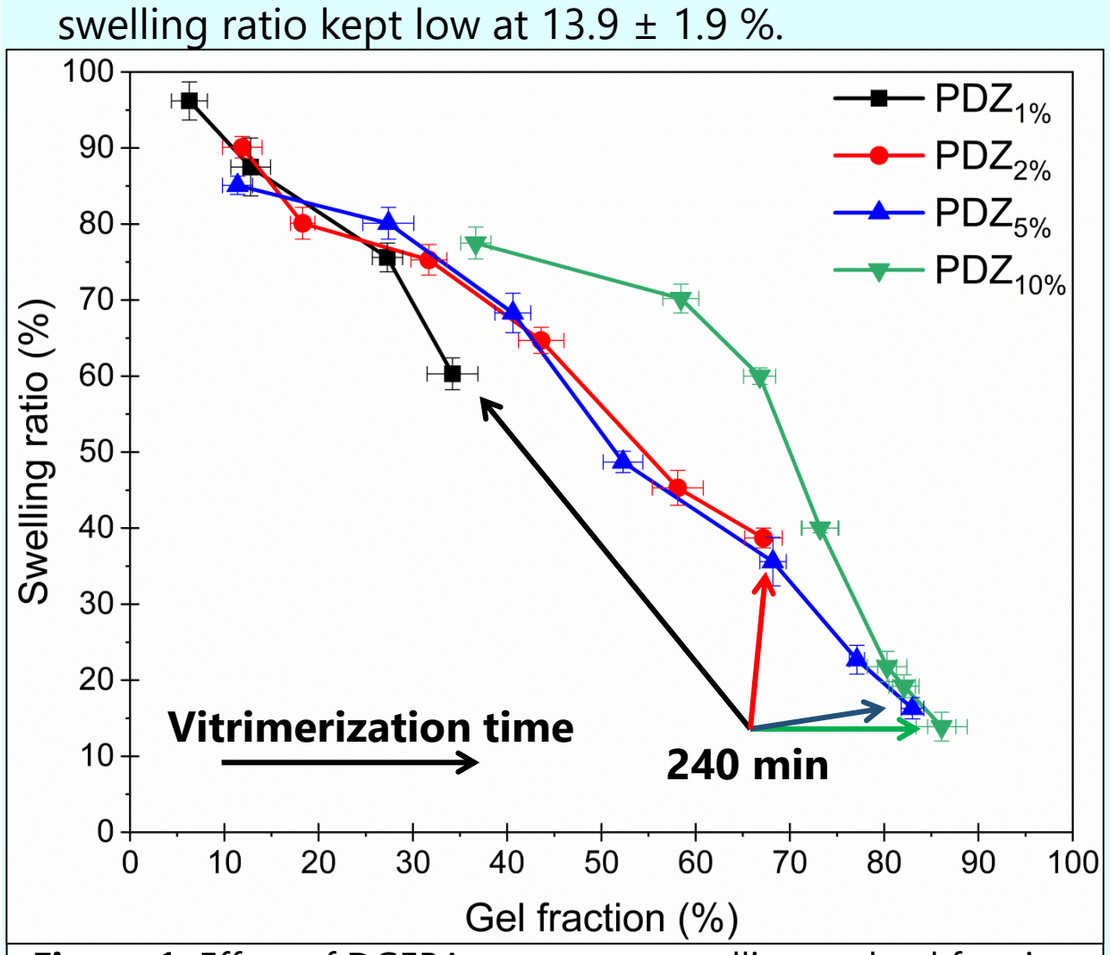


Figure 1. Effect of DGEBA content on swelling and gel fraction

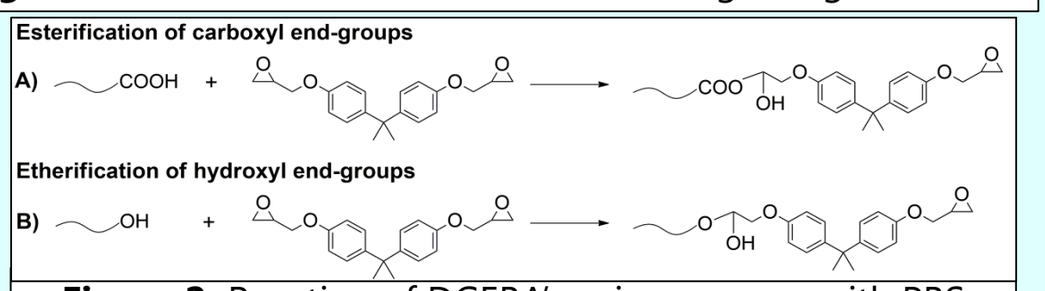


Figure 2. Reaction of DGEBA's oxirane group with PBS

Reprocessability

Cut to small pieces

Final vitrimer

Compression molding
190 °C, 30 min, 100 bar and cooling by water

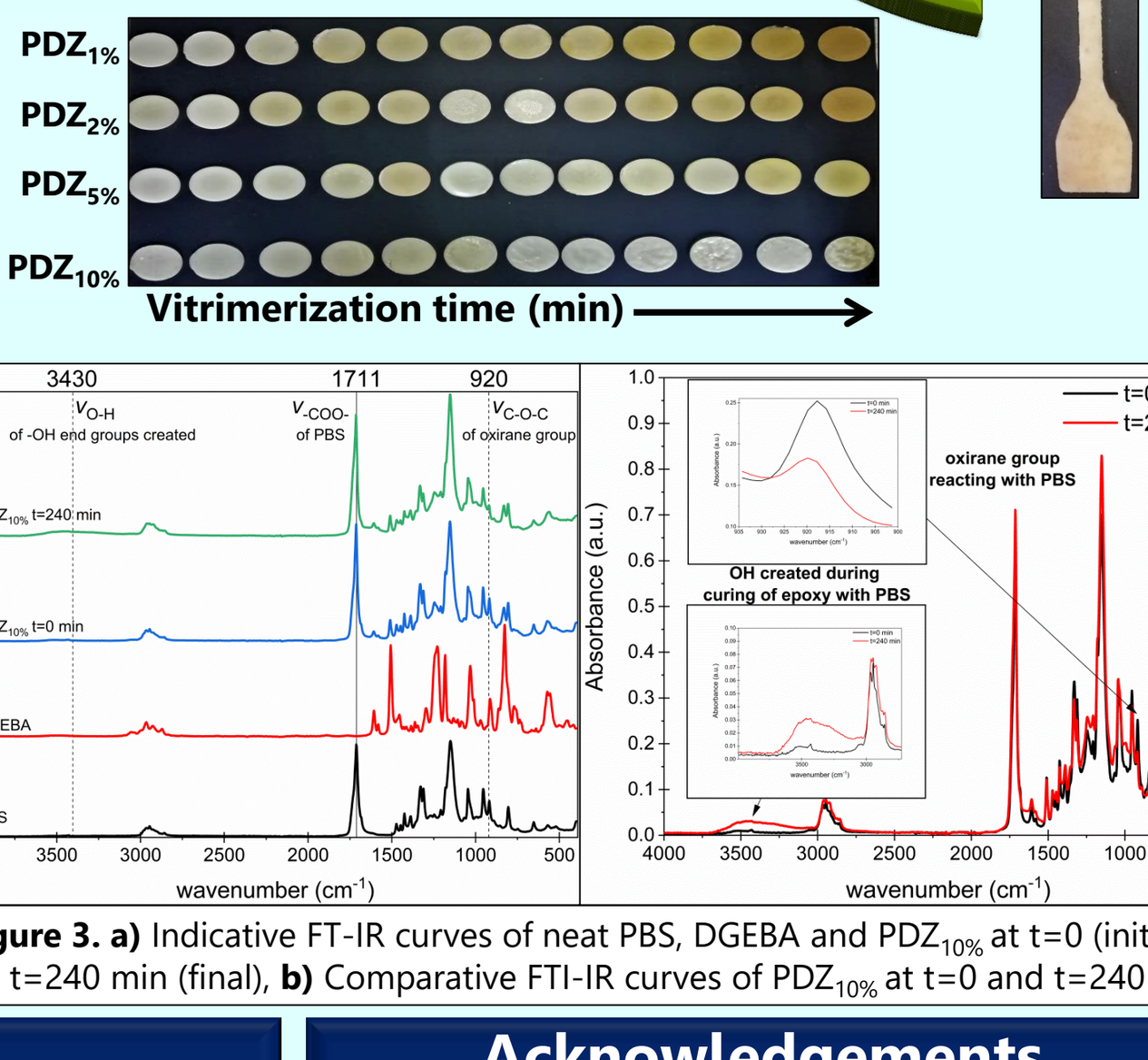


Figure 3. a) Indicative FT-IR curves of neat PBS, DGEBA and $PDZ_{10\%}$ at t=0 (initial) and t=240 min (final), **b)** Comparative FTI-IR curves of $PDZ_{10\%}$ at t=0 and t=240 min

References

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

[2] Hong et al. Future direction for sustainable polymers. Trends in Chemistry 2019;1(2):148-151.

Acknowledgements

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