Polymers for the Future

OST COFFEE LECTURES 2024

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Promote sustainability of polymer material using synthetic approaches

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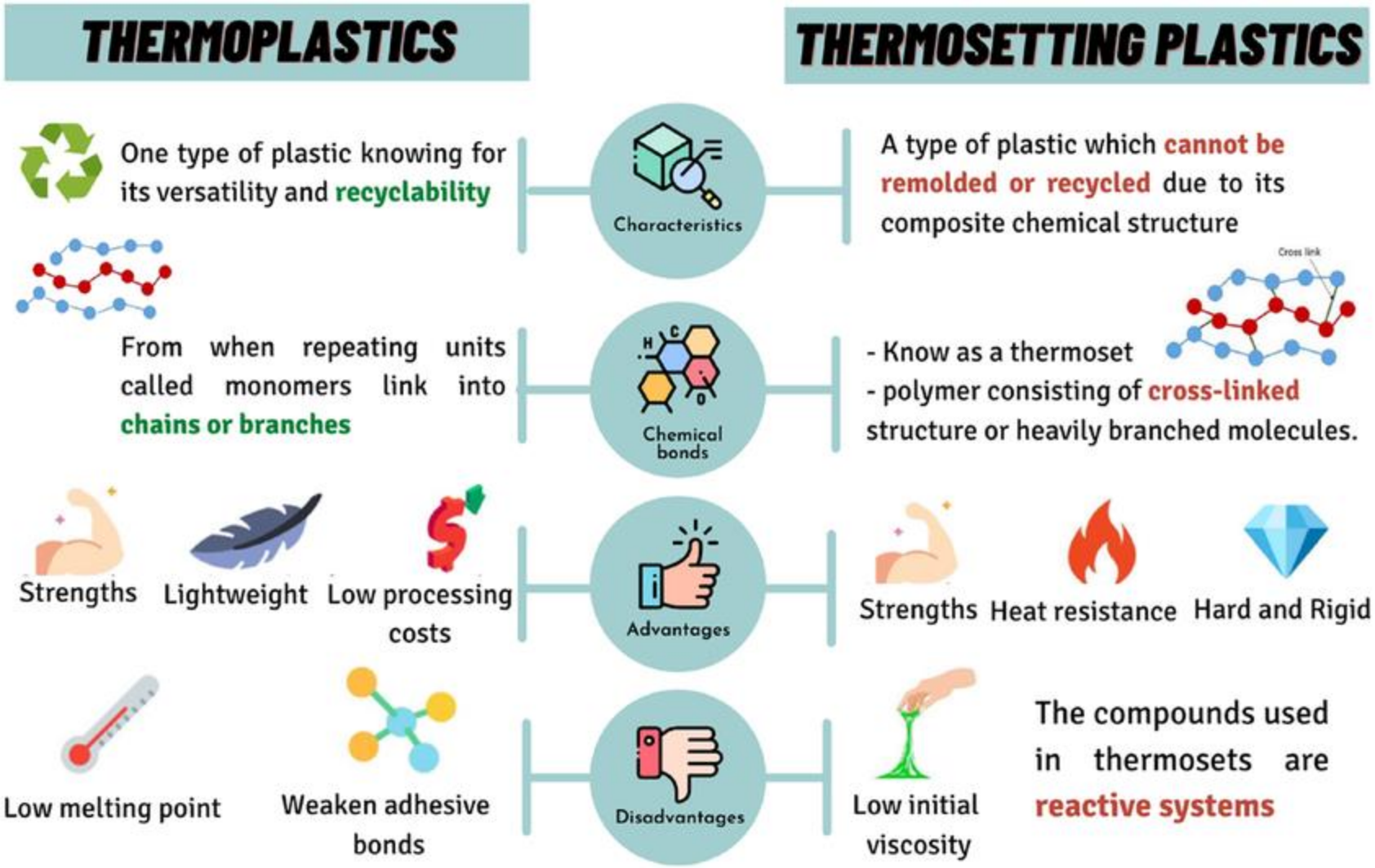
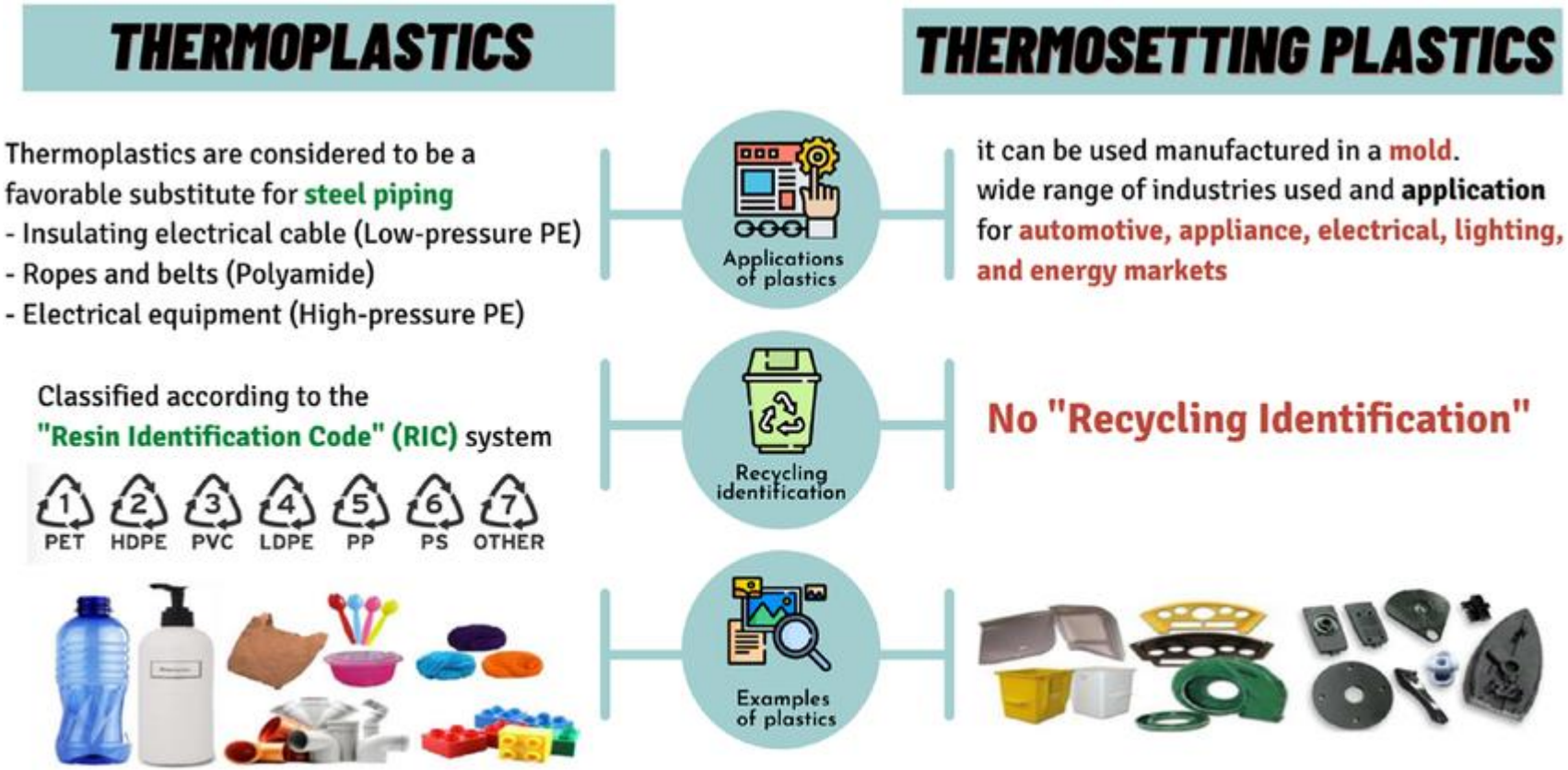
Background – Epoxy thermosets and EoL treatment



https://packagingeurope.com/features/how-new-solutions-for-recycling-thermoset-materials-are-providing-fresh-opportunities/8129.article
www.bulw.ifawg.org

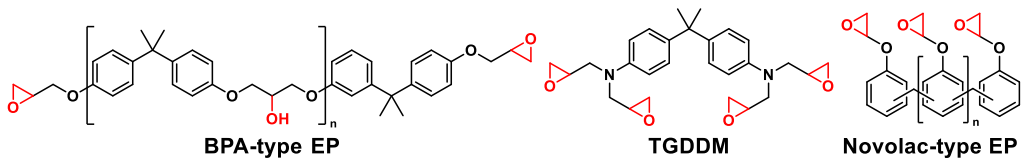
Background – Epoxy thermosets and EoL treatment



‘Global thermoset production in 2020: 42 million tonnes*’

- much based on Epoxy resins
- most recycled thermoset, polyurethane (2 million tonnes annually)

https://packagingeurope.com/features/how-new-solutions-for-recycling-thermoset-materials-are-providing-fresh-opportunities/8129.article



Background – Epoxy thermosets and EoL treatment

Based on Product*

- Primary Recycling: reprocessing to same/similar products
- Secondary Recycling: reprocessing to products with lower technical properties
- Tertiary Recycling: recovery of chemicals
- Quaternary Recycling: recovery of energy

Thermoplasts

- Mechanically recovereable after careful sorting,
- Polyester, polyamides and polyureathane or depolymerized,
- Remaining polymers require harsh uneconomical conditions

Thermosets

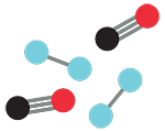
- Pyrolysis to fuels and hydrocarbon feedstock
- Grind to fillers

*Advanced Industrial and Engineering Polymer Research 4 (2021) 133-150

Based on Process**

Mechanical Recycling

Gasification



Pyrolysis

Solvent-based process

Depolymerisation

**Companies are placing big bets on plastics recycling. Are the odds in their favor? (acs.org)

Motivation – diverse solutions for EoL treatment and application requirement

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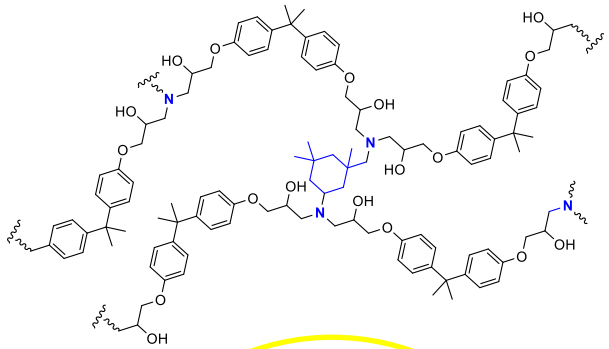
"Fixed" polymer network

- Epoxy cured with amine hardener
- C-C/C-N/C-O bonds



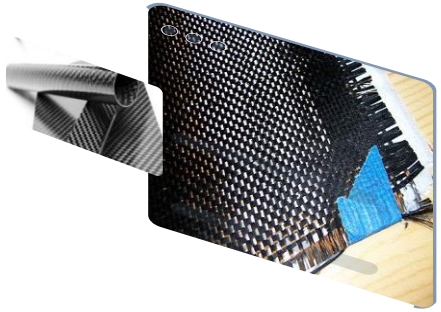
Thermoset:
low cost,
good mechanical properties,
high specific strength,
super adhesiveness,
good heat and solvent resistance

Non-recyclable/reprocessable,
Flammable,
Toxic smoke after ignition
…

*Both the thermoset matrix and its application - facing increasing **recycling demand** and **strict safety regulations***

Applications of epoxy thermoset

- Transportation: train, aviation, automotive …
- Electric Vehicles
- Construction
- Electronics

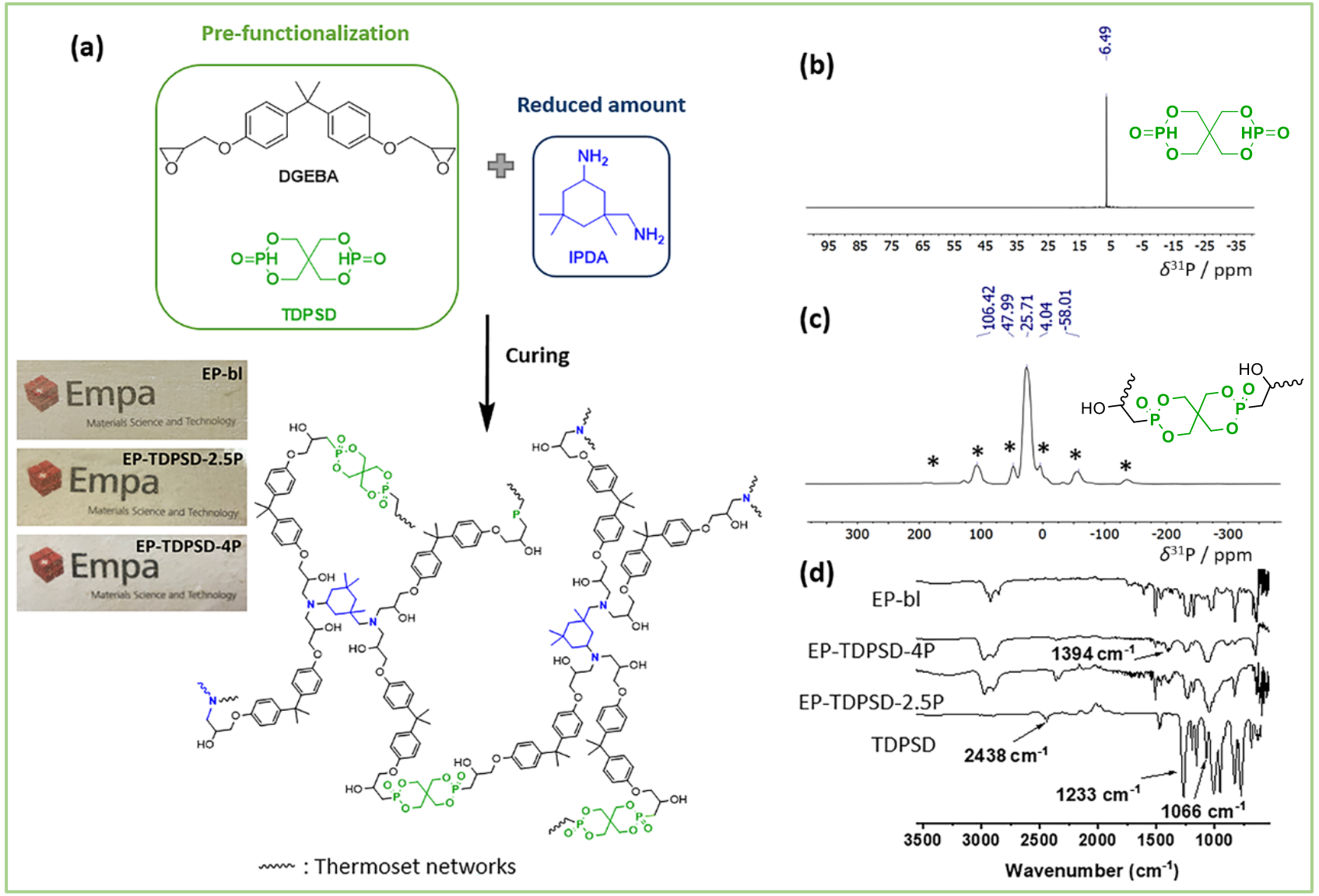


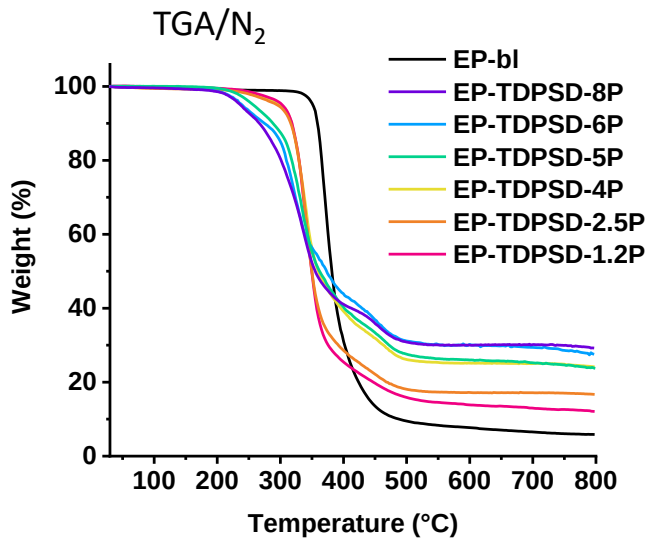
Aerospace standard CS 25.853 & FAR 25.853
Rail standard EN 45545
Electric vehicles UL2596 & UL94

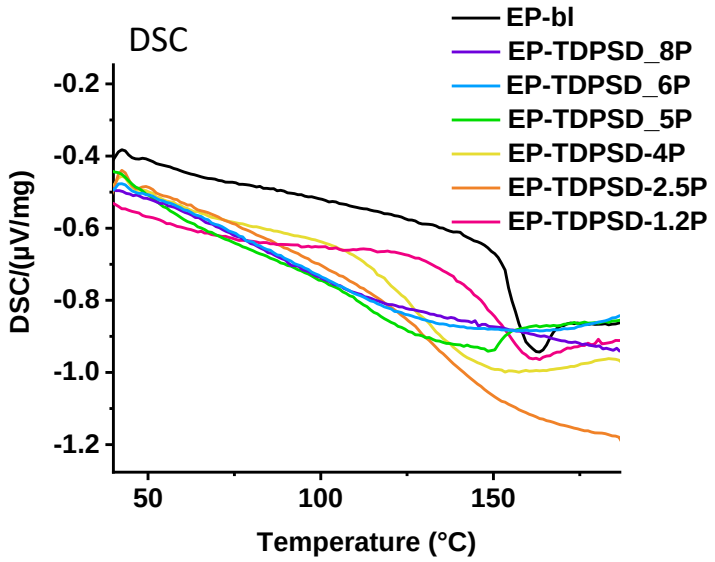
W. Wu Klingler, A. Bifulco, C. Polisi, Z. Huang, S. Gaan, Composites Part B: Engineering (2023) 110667.

Shieh, P.; Zhang, W.; Husted, K. E. L.; Kristufek, S. L.; Xiong, B.; Lundberg, D. J.; Lem, J.; Veysset, D.; Sun, Y.; Nelson, K. A.; et al. Nature 2020, 583 (7817), 542-547.

Introduction of “weak” bonds (CANs) with functionality - Phosphonated thermosets



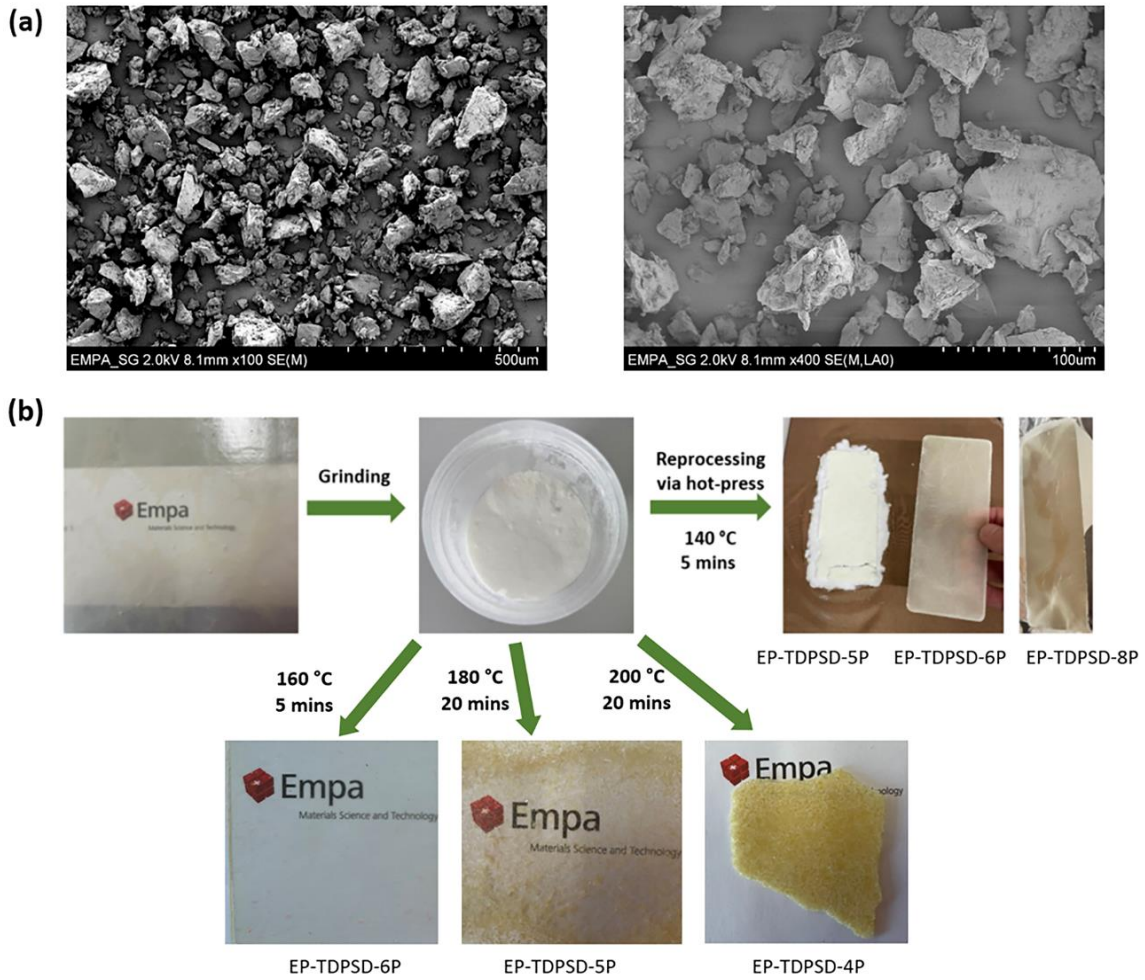




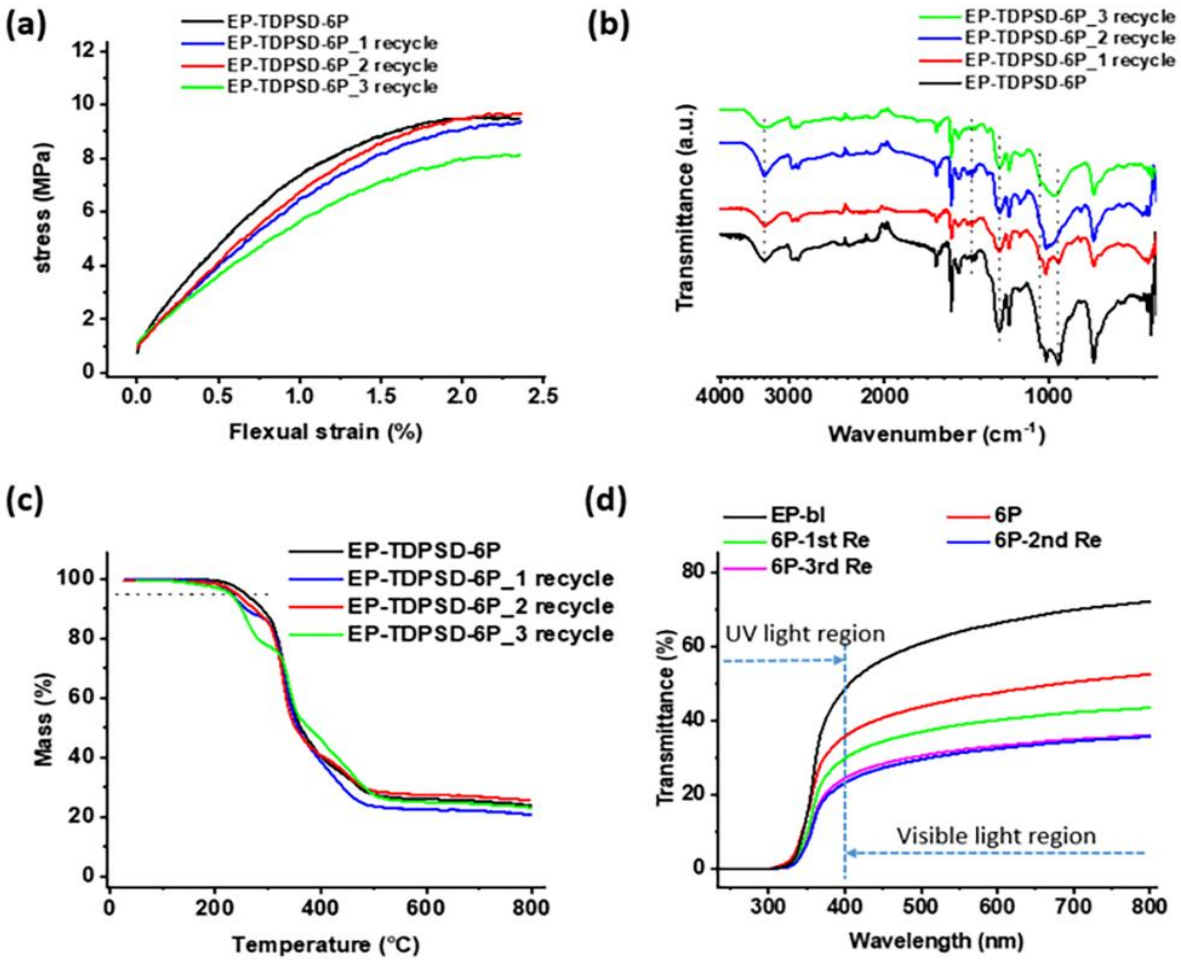
Empa Patent Application filed

W. Wu Klingler, V. Rougier, Z. Huang, D. Parida, S. Lehner, A. Casutt, D. Rentsch, K.B. Hedlund, G.A. Barandun, V. Michaud, S. Gaan, Chemical Engineering Journal 466 (2023) 143051.

Reprocessability of the Phosphonated thermosets



Solvent-free Grinding and pressing process: (a) SEM images of the cryo-grinded powder of EP-TDPSD-6P. (b) Under same hot-pressing condition (140 °C with up to 6 MPa pressure for 5 min) the outcomes of grinded EP-TDPSD-5P, EP-TDPSD-6P, and EP-TDPSD-8P samples

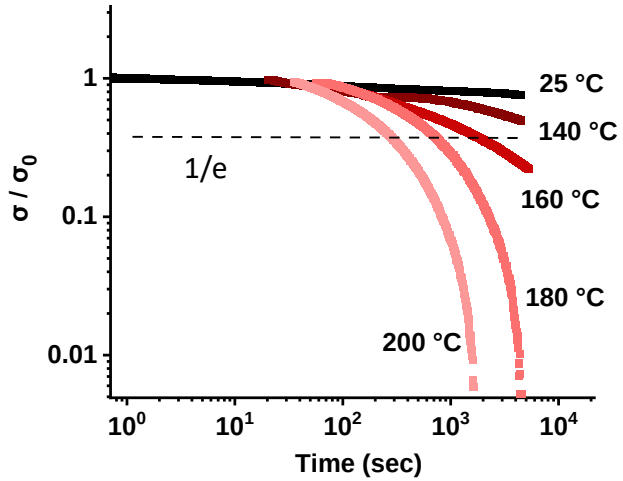


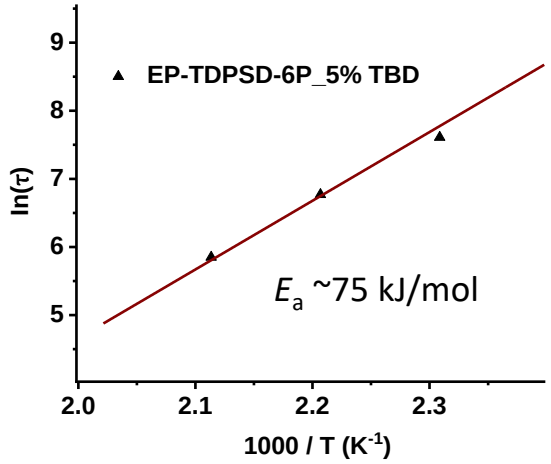
(a) Three-points bending, (b) FTIR, and (c) TGA results of the original and recycled EP-TDPSD-6P samples, in addition to (d) the UV–Vis light transmittance spectra of the visually transparent plates

Chemical Engineering Journal 466 (2023) 143051.

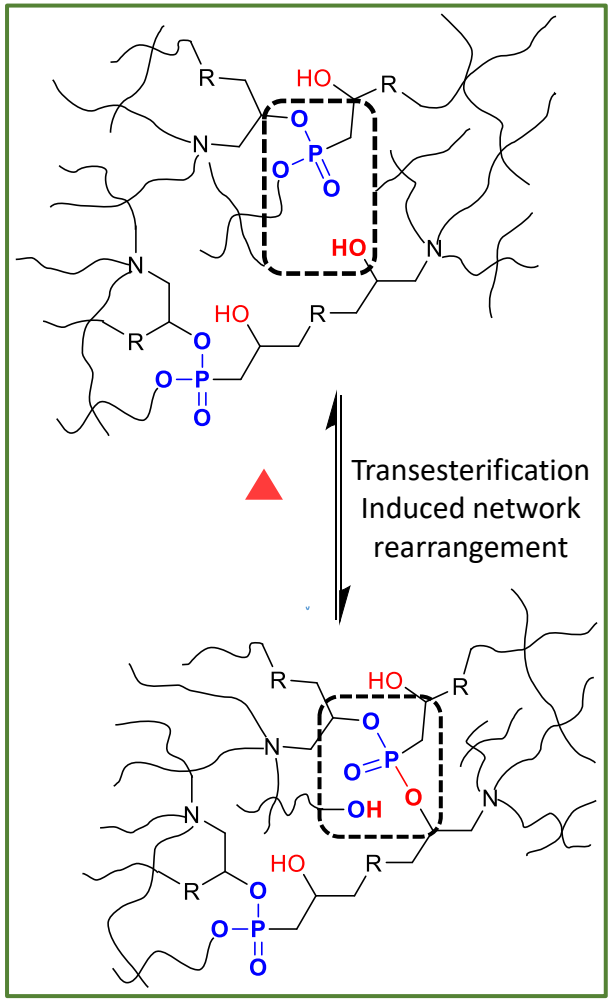
Reprocessability of the Phosphonated thermosets

Rheological stress relaxation





Transesterification induced network re-arrangement



Chemical recycling work Undergoing

Chemical Engineering Journal 466 (2023) 143051.

Flame retardancy of the Phosphonated thermosets

Fire-safety

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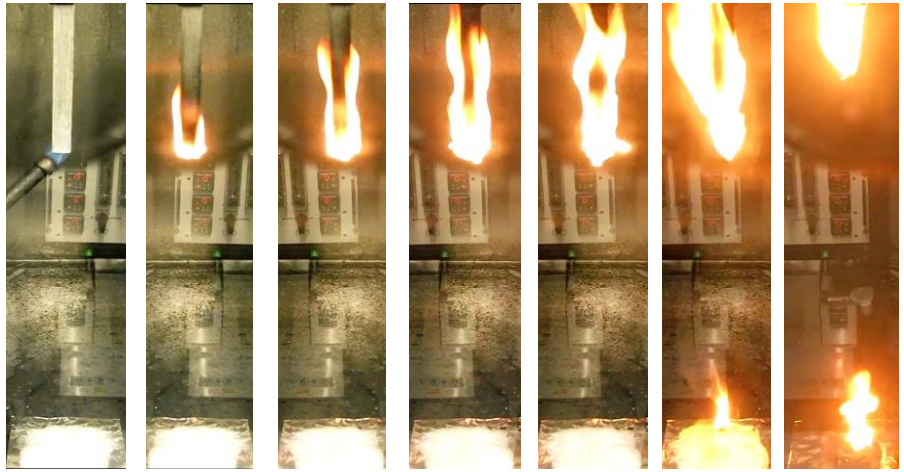
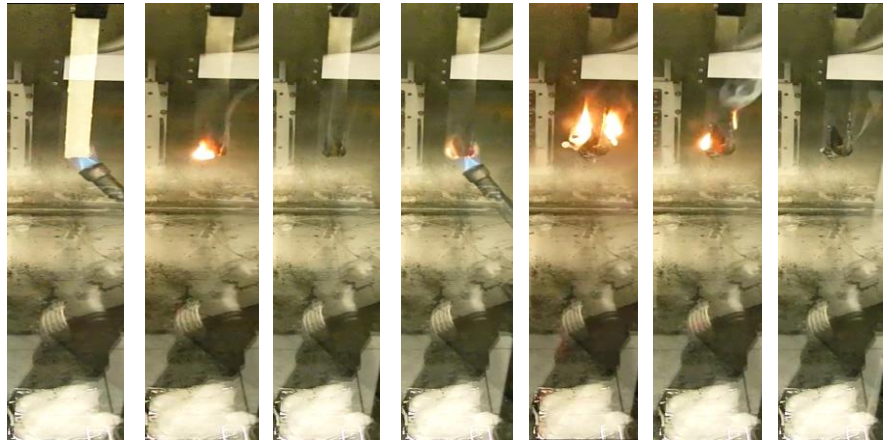
UL94 vertical burning test

EP-bl
No rate



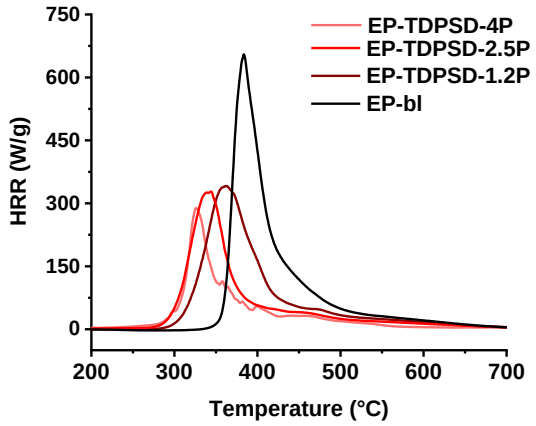
1st ignition 10s 20s 30s 40s 50s 100s

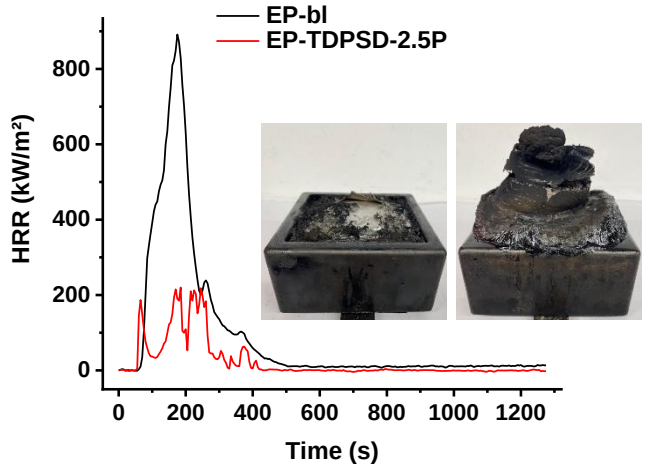
EP-TDPSD-2.5P
V0



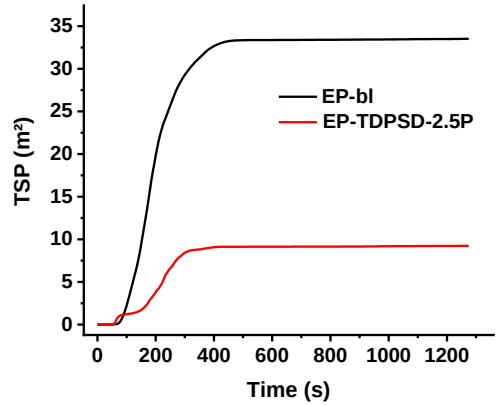
1st ignition 1s 3s 2nd ignition 1s 2s 3s

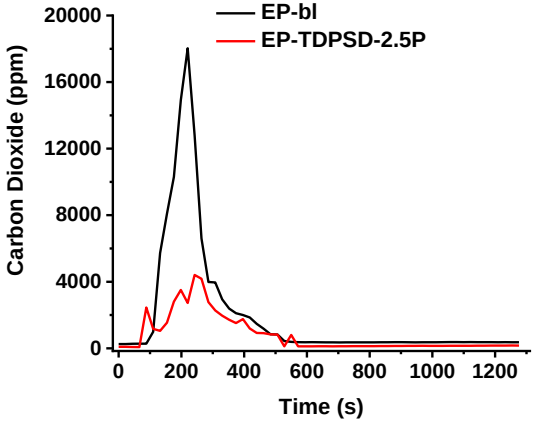
Heat release rate reduction





Smoke release reduction





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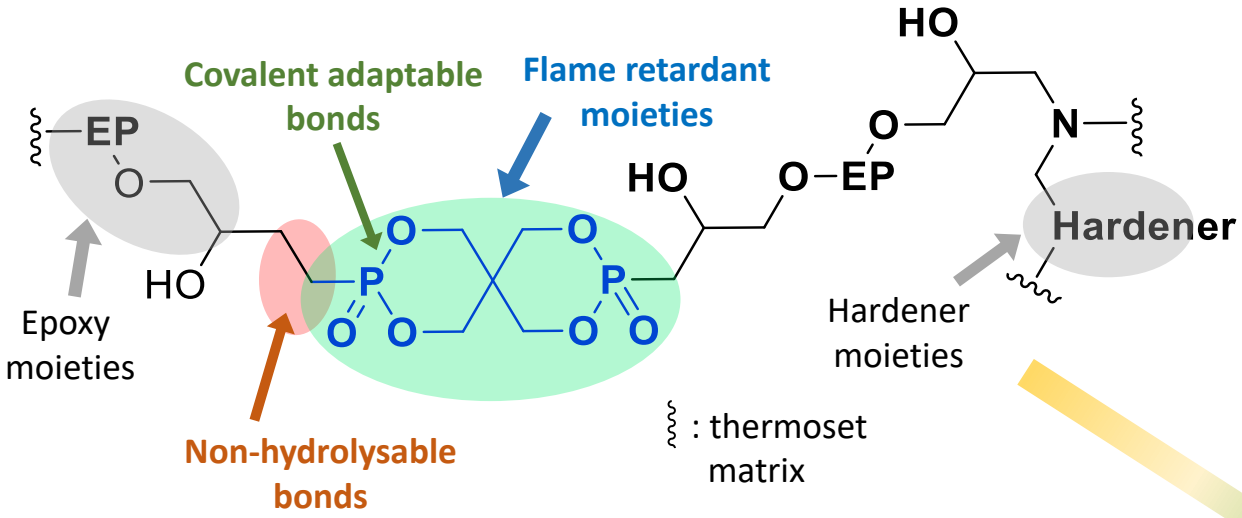
Introduction of “weak” bonds (CANs) with functionality – simpler phosphonated thermosets

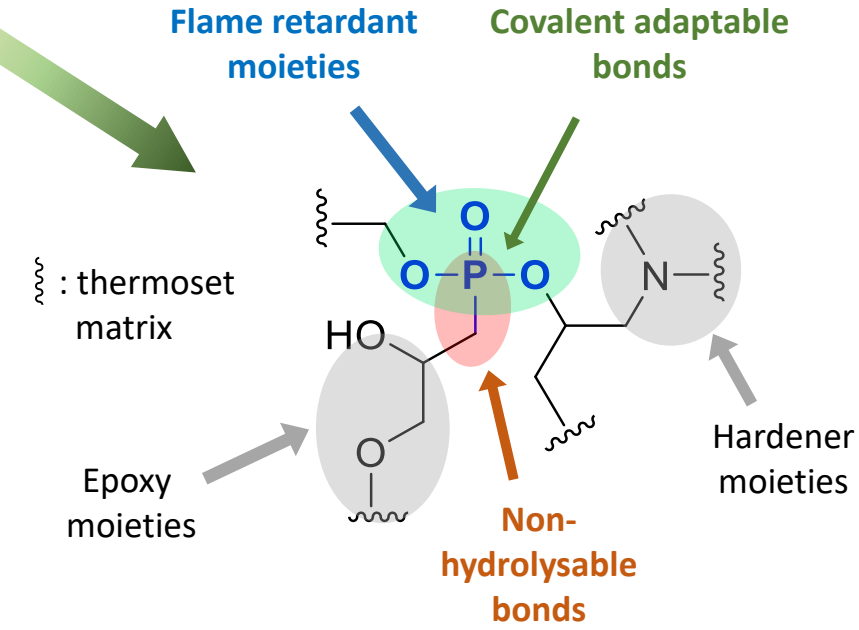


Target to **improve**:

- easier chemistry,
- more tunability,
- higher yield,
- Ideally neat reaction

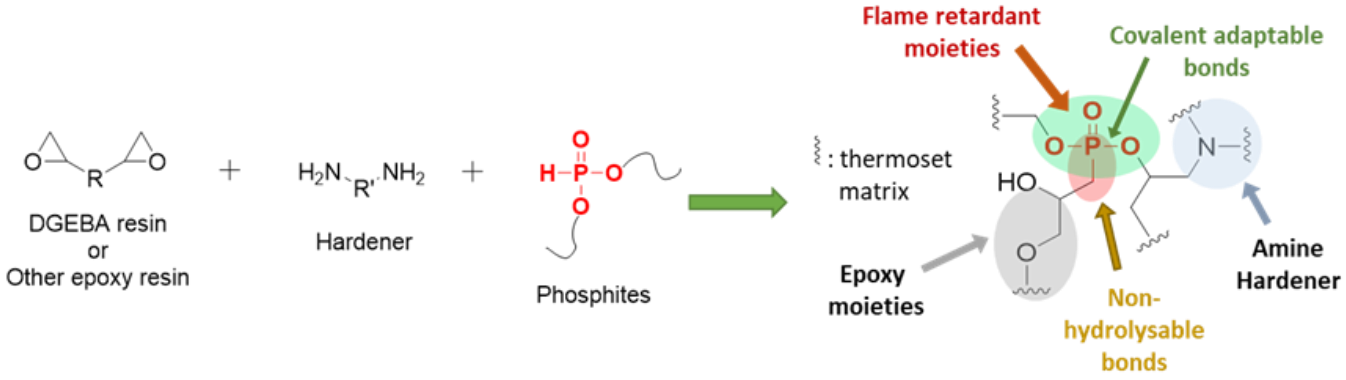
Certain **drawbacks** of the bis H-phosphite system:

- difficult to synthesize,
- 60% yield,
- using solvent,
- not stable monomer

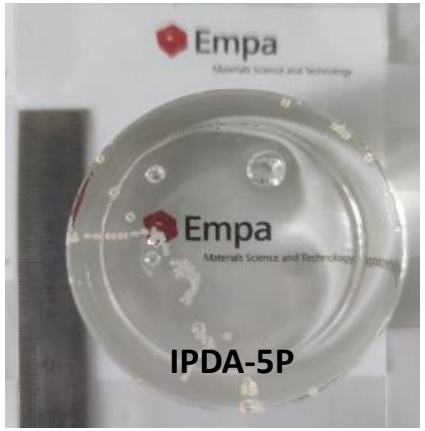


Simpler phosphite

One step synthesis using commercially available phosphite



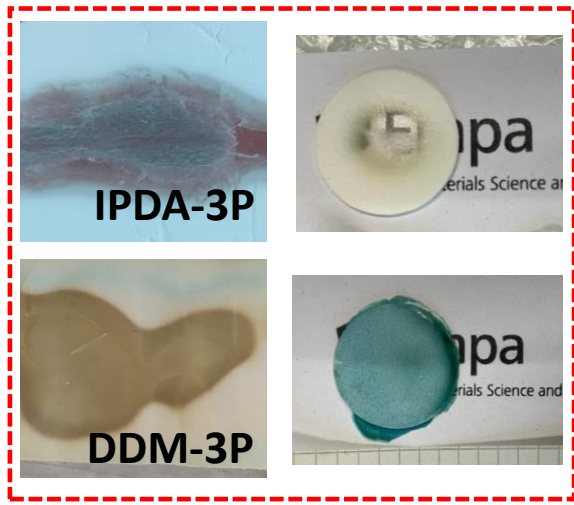
Reprocessability



Grinding

190 °C - 200
20 mins

Reprocessing via compresion molding



Flame retardancy

IPDA cured-3P
UL94 V0

DDM cured-3P
UL94 V0

Unpublished work

Application on flax fiber reinforced vitrimer composite (FRPC)

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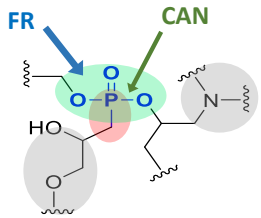
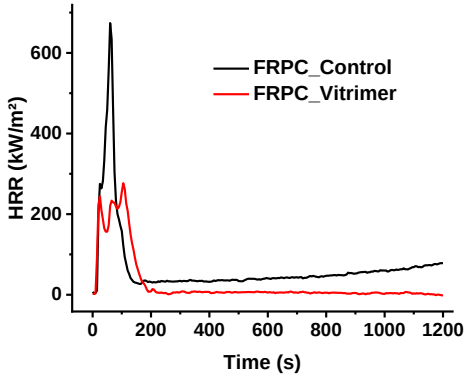
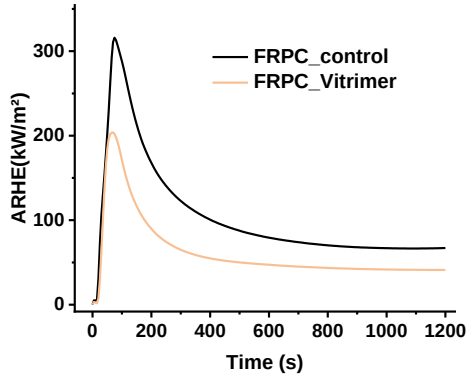
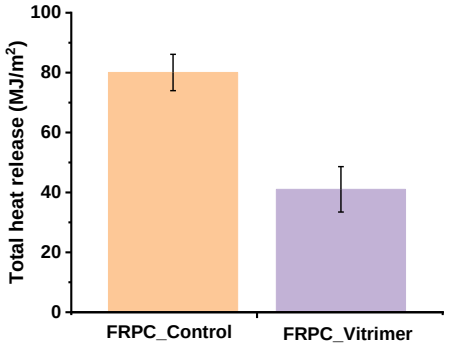
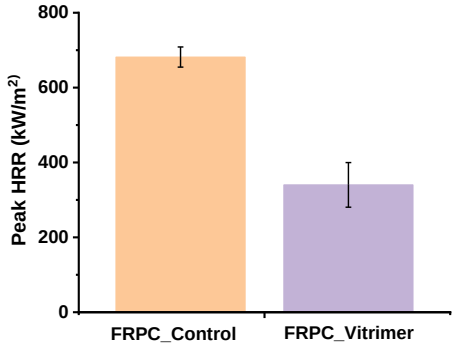
Combining Flame retardancy and Reprocessability







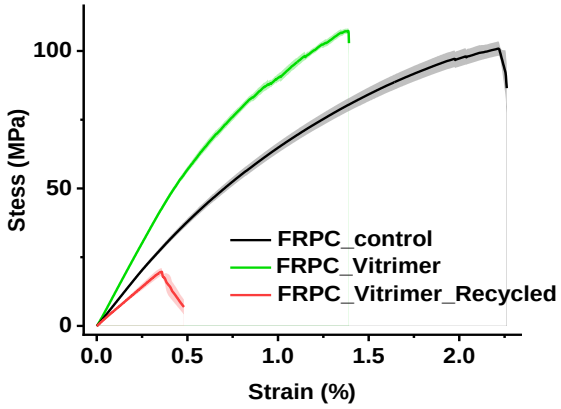




Multi-steps of shredding

Compression molding

Composite production waste



Recycled part

Unpublished work

Carboxylic ester based FR recyclable thermosets

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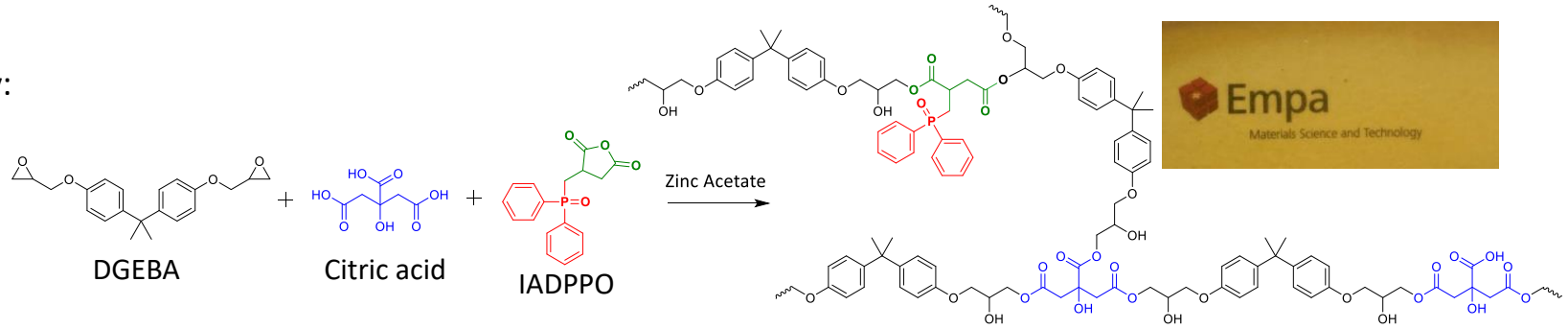
Synthesis pathway:

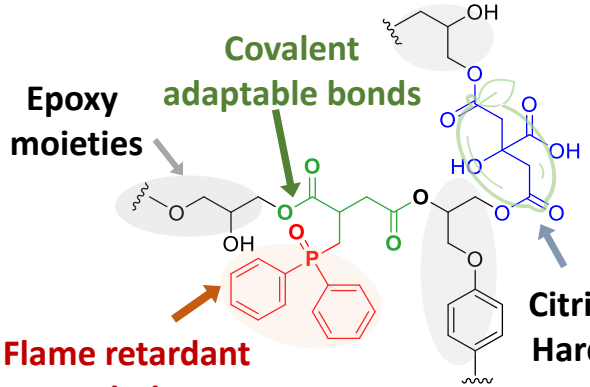


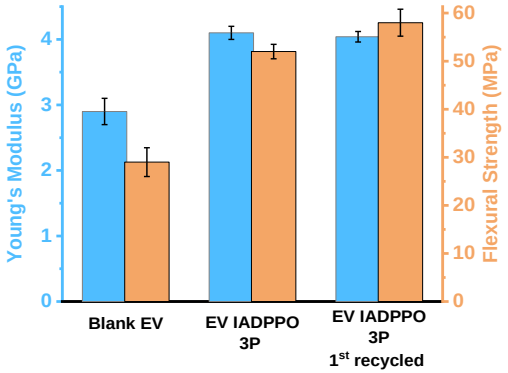
Overall performance:

Reprocessable

Hot press

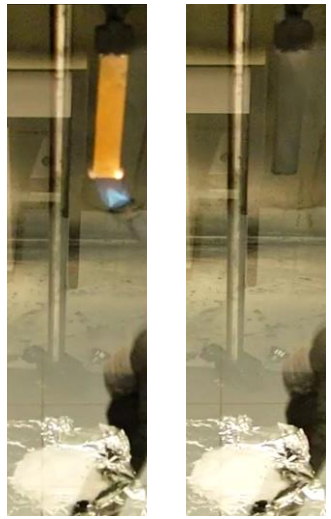
185 °C

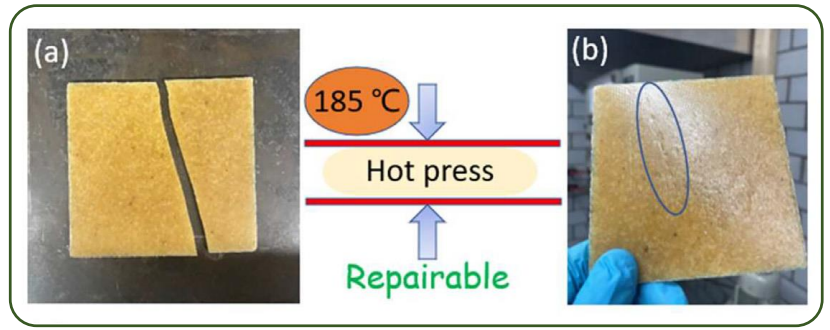


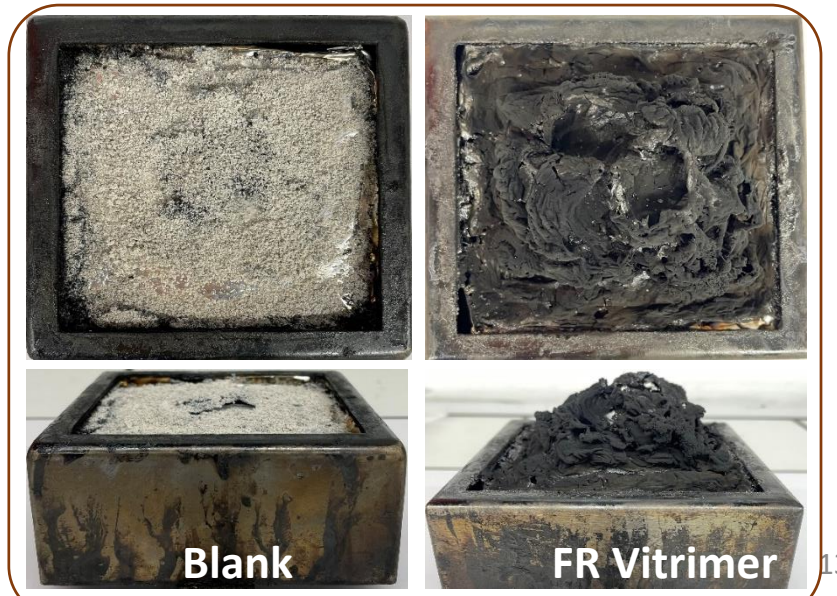


Mechanically Robust

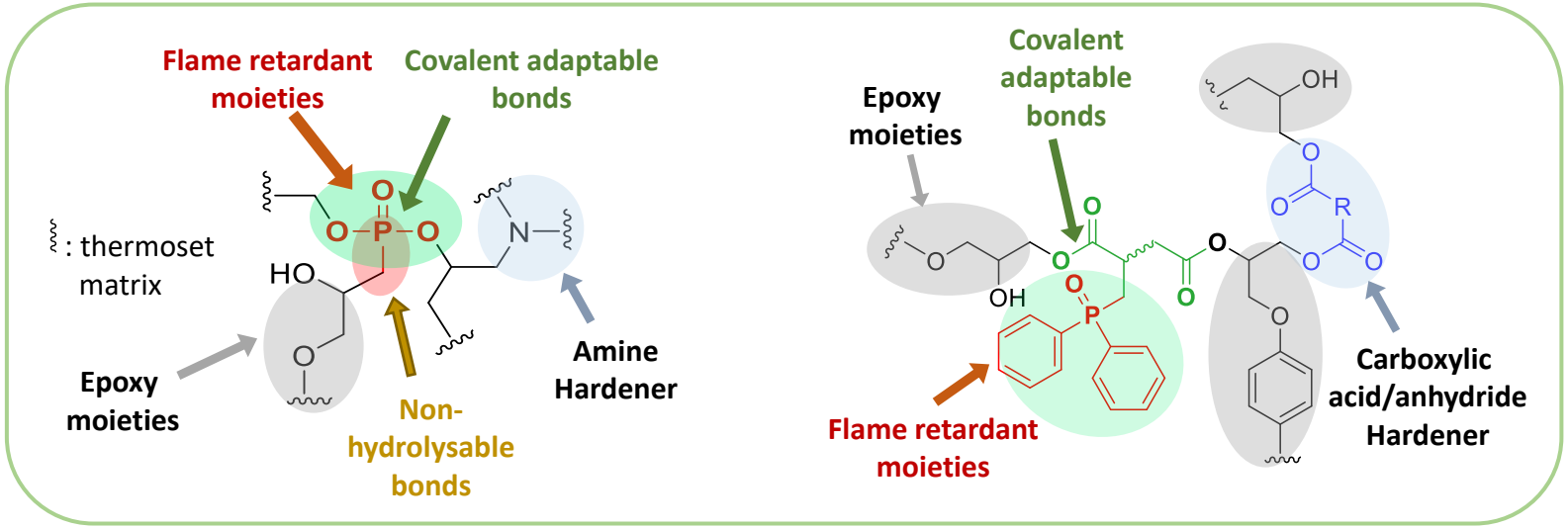
Flame-retardant

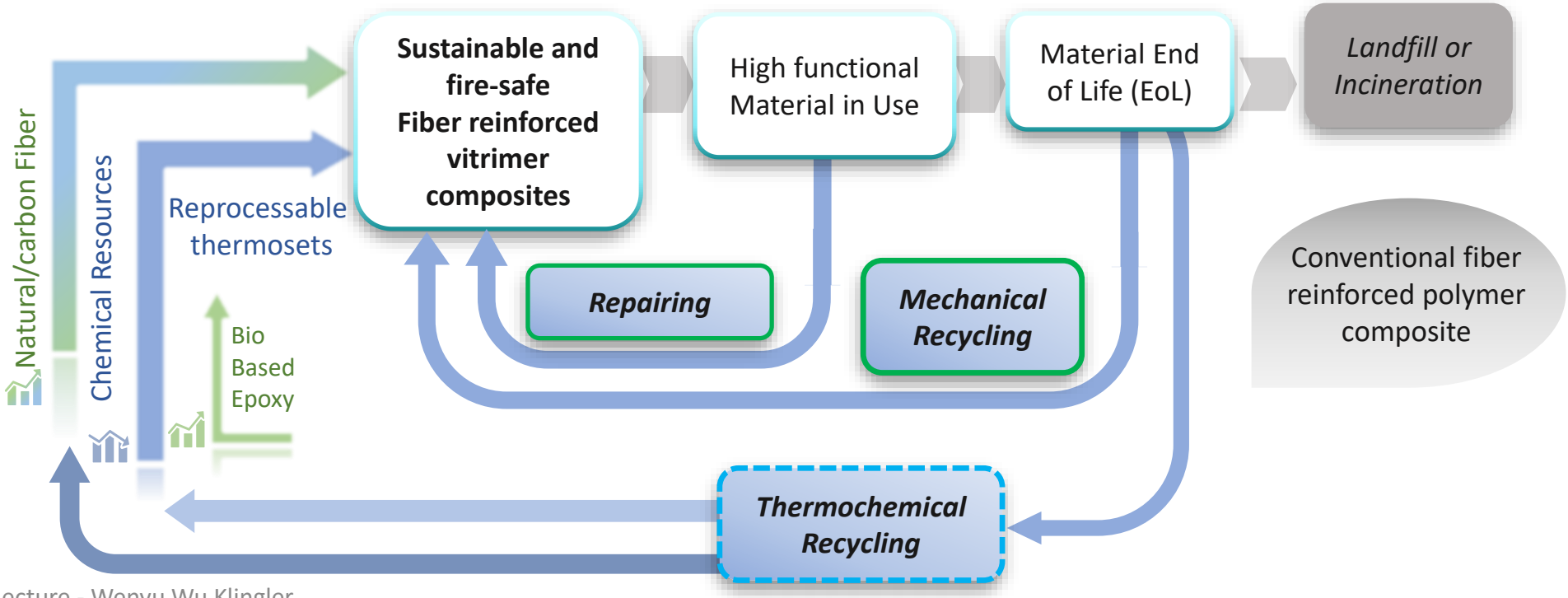






Summary - Recyclable Flame retardant Epoxy Thermosets and their application in FRPCs





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