Nachhaltige Kunststoffe in komplexen Anwendungen

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Enabling reprocessability and flame retardancy of epoxy thermosets via reactive approach

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INTRODUCTION

- Covalent adaptable networks (CAN) have exchangeable bonds embedded in the network, which enable thermoset material to be recycled (Figure 1).
- Flame-retardancy is another key concern for polymeric material application. Flame retardants are a crucial additives group in polymeric material, especially phosphorous-based ones [1].
- To achieve both of the desired properties, we developed phosphorus based monomeric/polymeric reactive curing reagent for epoxy thermosets.
- Vitrimer with phosphonate- and carboxylic-ester bonds containing CANs are developed (Figure 2).

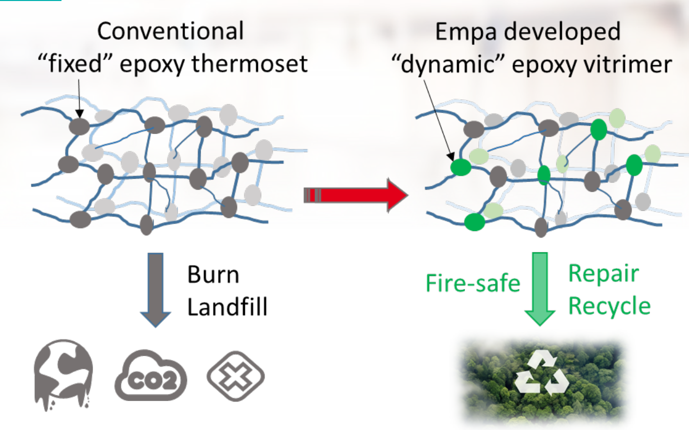

Figure 1: General comparison between our development with phosphonated dynamic network and conventional thermosets.

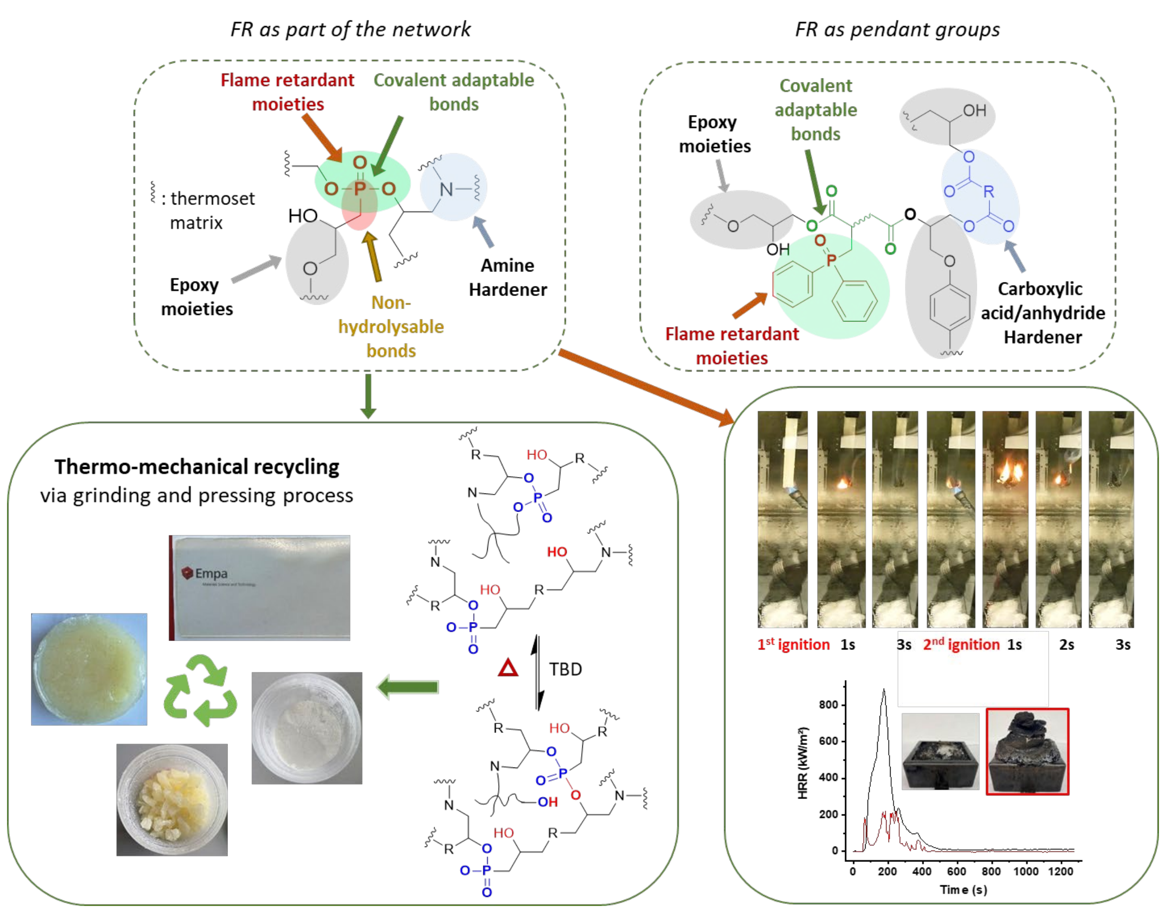

Figure 2: Schematic overview of the two approaches using phosphonate- and carboxylic-ester as CANs to achieve both recyclability and flame retardancy, with detailed results demonstrated from the phosphonated thermosets.

OBJECTIVE

Our work focuses on developing chemically feasible, recyclable and fire-safe thermosets based on phosphorus-containing reactive monomers [2]. Two types of CANs were obtained through the reaction of such monomers with epoxy resin, i.e. phosphonate ester bonds (Figure 2, up-left) [3] and carboxylic ester bonds (Figure 2, up-right).

Synthesis: Phosphorus containing reactive monomers were firstly developed as curing reagent for the multifunctional thermosets as shown in Figure 3.

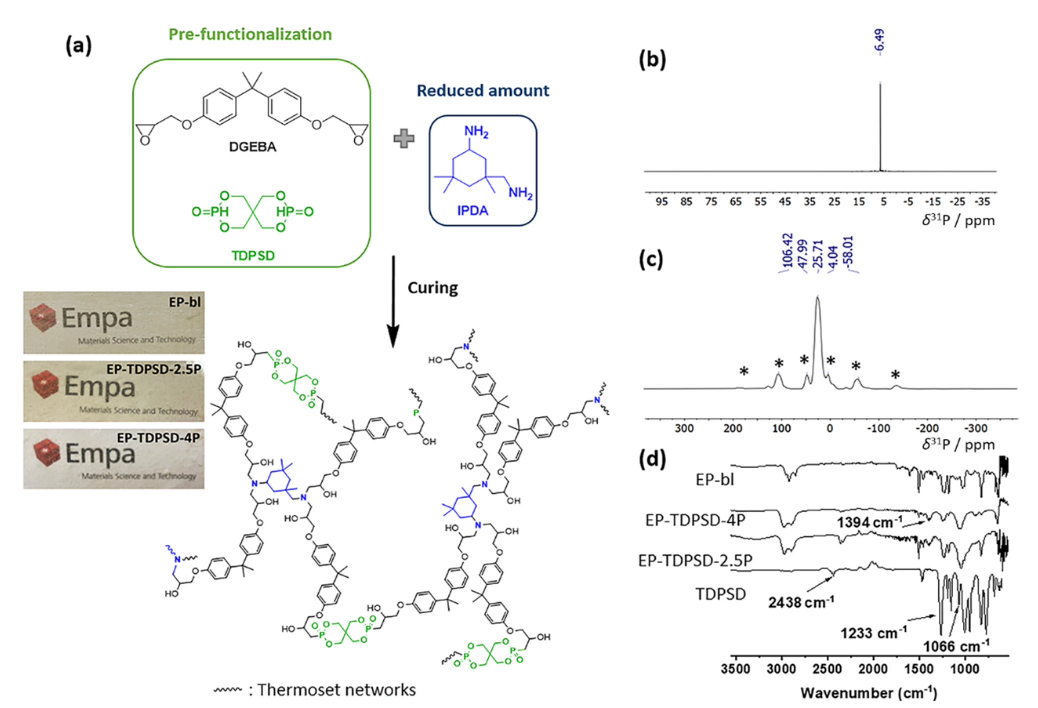

Figure 3: (a) Synthesis procedure of reactive phosphite cured epoxy thermosets. (b) ^{31}P NMR spectrum of bis H-phosphonate TDPSD in DMSO-d^6 solution, (c) solid state ^{31}P CP MAS NMR of EP-TDPSD-4P (* = spinning side bands), and (d) FTIR spectra of the thermosets.

Results and Conclusion:

Preliminary trials for coating and fiber reinforced polymer composites (FRPCs) were carried out to demonstrate the potential applications of the recyclable and fire-safe vitrimer like thermosets. Detailed recycling and fire-safe mechanism during combustion was investigated to provide guidance for further material design and developments (Figure 4).

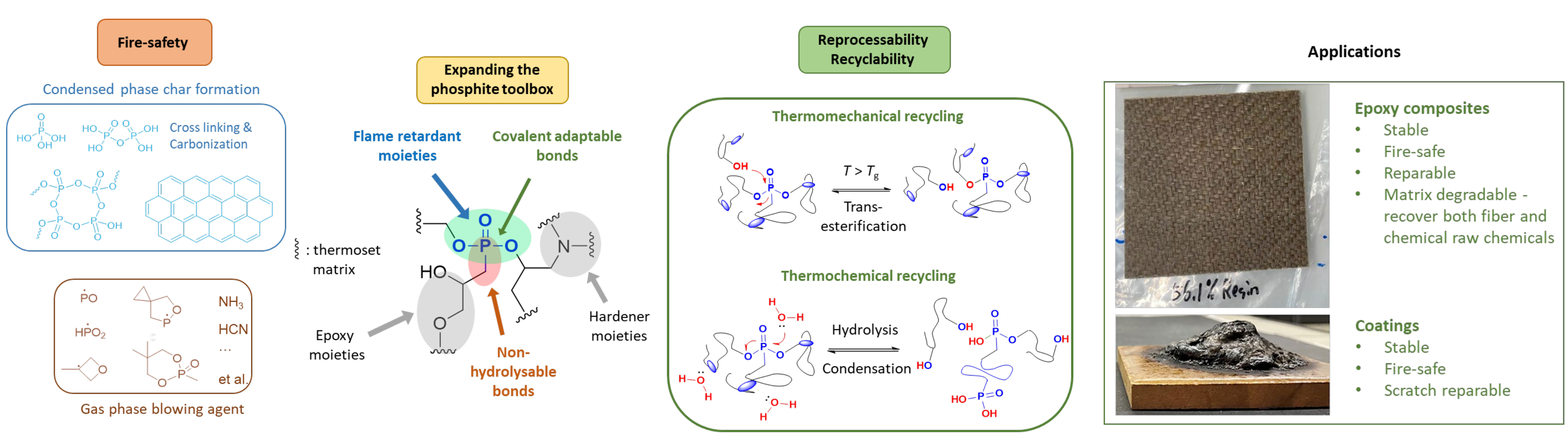

Figure 4: Summary of the fire-safe and recycling mechanisms for the phosphonate-ester thermoset system, with detailed explaination demonstrated in the middle. The potential applications are presented on the right side.

Excellent flame retardancy:

- 2.5 wt% P was essential to achieve good flame retardancy (UL94, Cone calorimeter, micro combustion calorimeter),
- TGA-FTIR, Pyrolysis-MS, DIP-MS confirmed the gas and solid phase fire inhibition actions.

Recyclability:

- 5 wt% P is sufficient for good thermomechanical recyclability,
- Catalysts promoted transesterification between the ester bonds and the abundant hydroxyl groups,
- Hydrolysis or alcoholysis could be used for full chemical recycling.

ACKNOWLEDGEMENTS

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