CAN-containing epoxy vitrimers – thermoset polymers with inherent recyclability

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Introduction

Thermoset polymeric composites are widely used in almost every industrial sector (construction, aeronautics, automotive, renewable energy, sports) where both lightness and great mechanical performance are required. For the most demanding applications, epoxy resins are used as a composite matrix because of their excellent physical, mechanical, and thermal properties. The major disadvantage of cured epoxy resin and its composites is the difficulty in recycling them due to their thermoset nature. An answer to this issue are epoxy vitrimers, which represent a new group of polymers combining the excellent mechanical properties of thermosets with the reprocessability of thermoplastics. These materials address the challenges of recycling and processing traditional thermosetting plastics and serve as bridging materials between thermosetting and thermoplastic polymers. Vitrimers, through the introduction of covalent adaptable bonds (CAN), maintain chemical and mechanical stability under normal conditions (Fig. 1). However, under specific stimuli, these bonds have the ability to break and reform, enabling the possibility of reprocessing or self-healing of the crosslinked epoxy polymers.

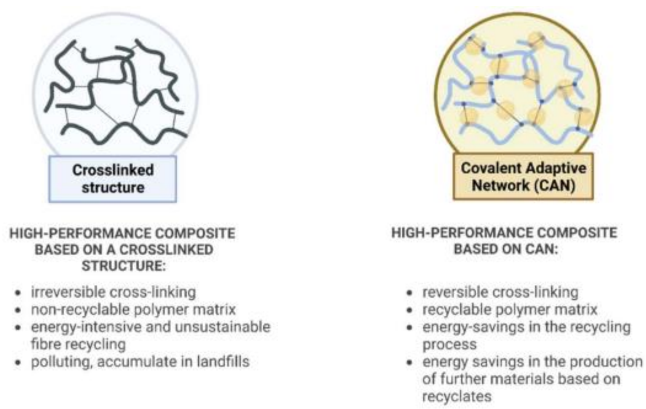

Figure 1. *Main differences between traditional and CAN-containing composites*

In the present study a low-molecular weight epoxy resin cured with carboxylic acids or acid anhydrides was modified with a series of catalysts imparting CAN's into polymer structure. In the ESTELLA project epoxy vitrimers will be used as a matrix for composites reinforced with functionalized lignocellulosic nanofibres or functionalized natural fibre yarns and oriented textiles. As a result of the project realization, epoxy composites with inherent recyclability will be developed.

Experimental

Epoxy vitrimers were obtained by curing of low-molecular weight epoxy resin with carboxylic acids or acid anhydrides in the presence of amine CAN catalysts, in the elevated temperatures. Recyclability of vitrimers was proven by dissolving of cured materials in the solvents containing hydroxyl groups. Properties of virgin and recycled products were characterized by FTIR and TG analyses.

Results and Discussion

FTIR spectra of vitrimer synthesis in the reaction of epoxy resin with citric acid as crosslinking agent showed disappearance of the band at 863 and 915 cm^{-1}, corresponding to epoxy ring vibrations, carboxyl band at 1705 cm^{-1}, and forming of the band at 1732 cm^{-1}, characteristic for ester groups (Fig. 2). Product obtained with amine CAN catalyst underwent dissolution in solvent. Comparison of TG curves of virgin resin sample with recycled sample (after solvent evaporation, Fig 3.) showed very little deterioration of material properties.

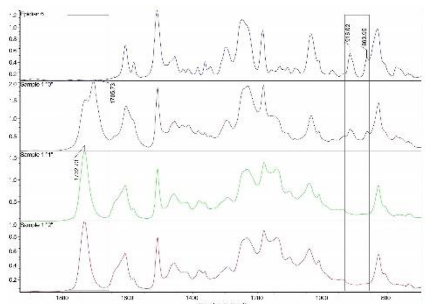

Figure 2. *Progress of reaction measured by FTIR*

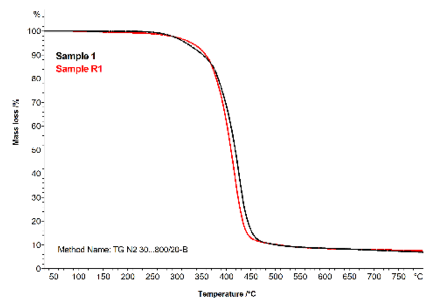

Figure 3. *TG curves of virgin (1) and recycled (R1) vitrimer*

Conclusions

Epoxy vitrimers are very promising polymers, designed to have dynamic and reversible bonds, allowing efficient recycling of waste materials. The study demonstrates the successful synthesis of epoxy vitrimers with inherent recyclability, using low-molecular weight epoxy resin, acids or anhydrides, and amine CAN catalysts. The vitrimers showed recyclability through dissolution in solvents and exhibited promising properties, as indicated by FTIR and TG analyses.

Acknowledgments:

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Biography

Damian Kiełkiewicz is the Leader of Advanced Materials Research Group at Institute of Heavy Organic Synthesis "Blachownia", a member of Łukasiewicz Research Network. He was graduated at Opole University and completed postgraduate studies at Stanford University. His main research area comprises technologies of epoxy resins, phenolic resins and non-isocyanate polyurethanes. Co-author of 3 papers and 27 patents, mostly implemented into industrial practice.