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Build-to-Spec. Bio-based Building-Blocks for Thermosets Materials

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PURPOSE OF THE ABSTRACT

SPECIFIC POLYMERS (SP - www.specificpolymers.fr) is a SME with 17 employees acting as R&D service provider and intermediate scale-up producer in the field of functional building-blocks, polymers and materials with high specificity. The main goal of the innovative products developed by SPECIFIC POLYMERS is to validate proof of concepts and develop tomorrow's materials. In this context, green material chemistry and biomass valorization is a fundamental aspect of SP research and development activities. Many industrial and collaborative projects are ongoing to find bio-based alternatives to fossil resources having an industrial viability. In this scope, SP research efforts are mainly dedicated to (Figure 1):

(i) Bio-based alternative building-blocks to substitute toxic and petro-based Diglycidyether of Bisphenol-A in epoxy resins.

(ii) Cyclocarbonates for the synthesis of polyhydroxyurethanes to substitute toxic isocyanate base polyurethane materials.

(iii) Bio-based alternative building-blocks to substitute toxic phenol and formaldehyde in formophenolic resins.

(iv) End-of-life phase of thermoset materials that suffer from a lack of reprocessability, reparability and recyclability.

The research activity proposed by the company aimed at the development of innovative resins that fulfill all customer's specifications in terms of process and final properties (i.e. Build-to-Spec. resins). Development processes are mainly based on experimental researches but the company is moving toward the integration of numerical modeling into its material development chain.

Among all R&D project of the company in the field of bio-based materials, a special attention will be given to bio-based epoxy building-blocks that can be used for the substitution of Diglycidylether of Bisphenol A (DGEBA) into epoxy-amine materials. Alternative bio-based building-blocks were synthesized and tailor-made according to the requirements of involved processes (RTM, Pultrusion, Impregnation) and taking into account the specification of end users in applications as different as automotive, building industry or aeronautic.

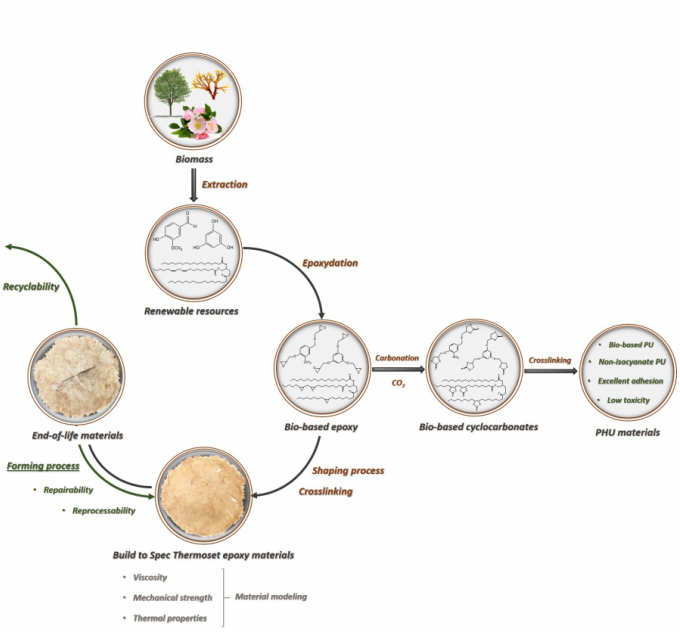
In these areas, a representative study was dedicated to (i) the synthesis of Vanillin DiGlycidylEther (DGEVA) prepared from vanillyl alcohol that can be extracted from lignin[1] and to (ii) Phloroglucinol TriGlycidylEther (Phloroglucinol-TGE - PHTE) that can be extracted from algae[2,3] (Figure 2). Both epoxy resins are aromatic

multifunctional glycidyl ethers that can be combined to reach a range of thermomechanical properties.

It was proved in this work that it was possible to reach the specifications of forming processes and end-users by adjusting the DGEVA/PHTE mixture. Such epoxy building-block are thus very promising to substitute DGEBA resins in corresponding application. Based on this, this R&D project now aims at producing 50 to 100 kilograms of the most suitable resins for deeper evaluation in aforementioned sectors. As a consequence, a significant part of the work is dedicated to synthesis process optimization to reach a viable product for these markets.

Another case study concerns the epoxidation of various vegetable oils[4] (Figure 2). The degree of unsaturation and the chemical nature of vegetable oils have a great influence on reachable epoxidation degree and thus final epoxy resin properties. A particular attention was also given to the influence of the epoxy index, the molecular weight and the epoxy reactivity of synthesized precursors on resins processability and thermomechanical properties. Researches are underway.
Finally, reparability, reprocessability and recyclability properties were highlighted for thermoset composite materials obtained from developed bio-based epoxy resins combined with dynamic hardeners[5].

FIGURES



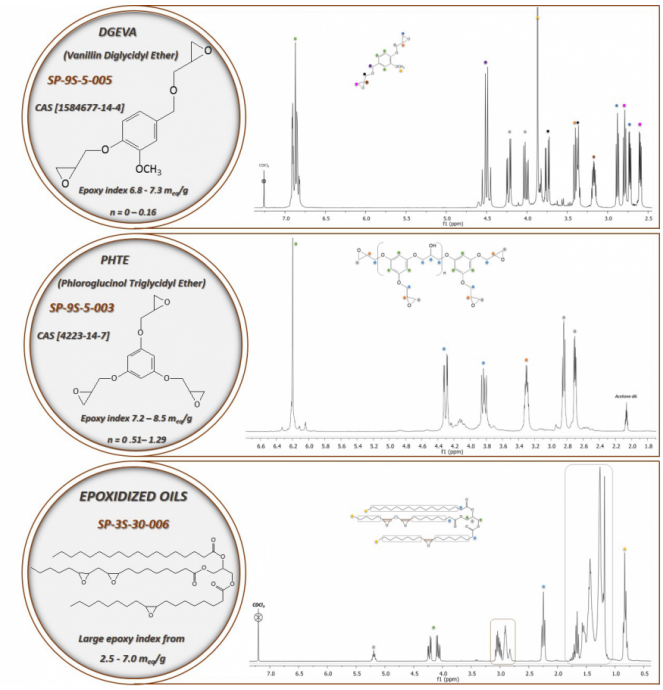


FIGURE 1

Figure 1

SPECIFIC POLYMERS strategy for the development of thermoset materials

FIGURE 2

Figure 2

Bio-based Building-Blocks for Thermoset Epoxy resins

KEYWORDS

Bio-based Epoxy Resins | Composite Materials | Recyclable bio-based thermosets | Biomass valorization

BIBLIOGRAPHY

[1] M. Fache, B. Boutevin and S. Caillol, Epoxy thermosets from model mixtures of the lignin-to-vanillin process, Green Chem., 2016, 18, 712

[2] J. Ding, O. ur Rahman, W. Peng, H. Dou and H. Yu, A novel hydroxyl epoxy phosphate monomer enhancing the anticorrosive performance of waterborne Graphene/Epoxy coatings, Applied Surface Science 427 (2018) 981–991

[3] Pal Singh, I., & Bharate, S. B. (2006). Phloroglucinol compounds of natural origin. Natural Product Reports, 23(4), 558

[4] S. M. Danov, O. A. Kazantsev, A. L. Esipovich, A. S. Belousov, A. E. Rogozhin and E. A. Kanakov, Recent advances in the field of selective epoxidation of vegetable oils and their derivatives: a review and perspective, Catal. Sci. Technol., 2017, 7, 3659

[5] A. Ruiz de Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabañero, J. Rodríguez and I. Odriozola, Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites, Mater. Horiz., 2016, 3, 241-247