SPECIFIC POLYMERS

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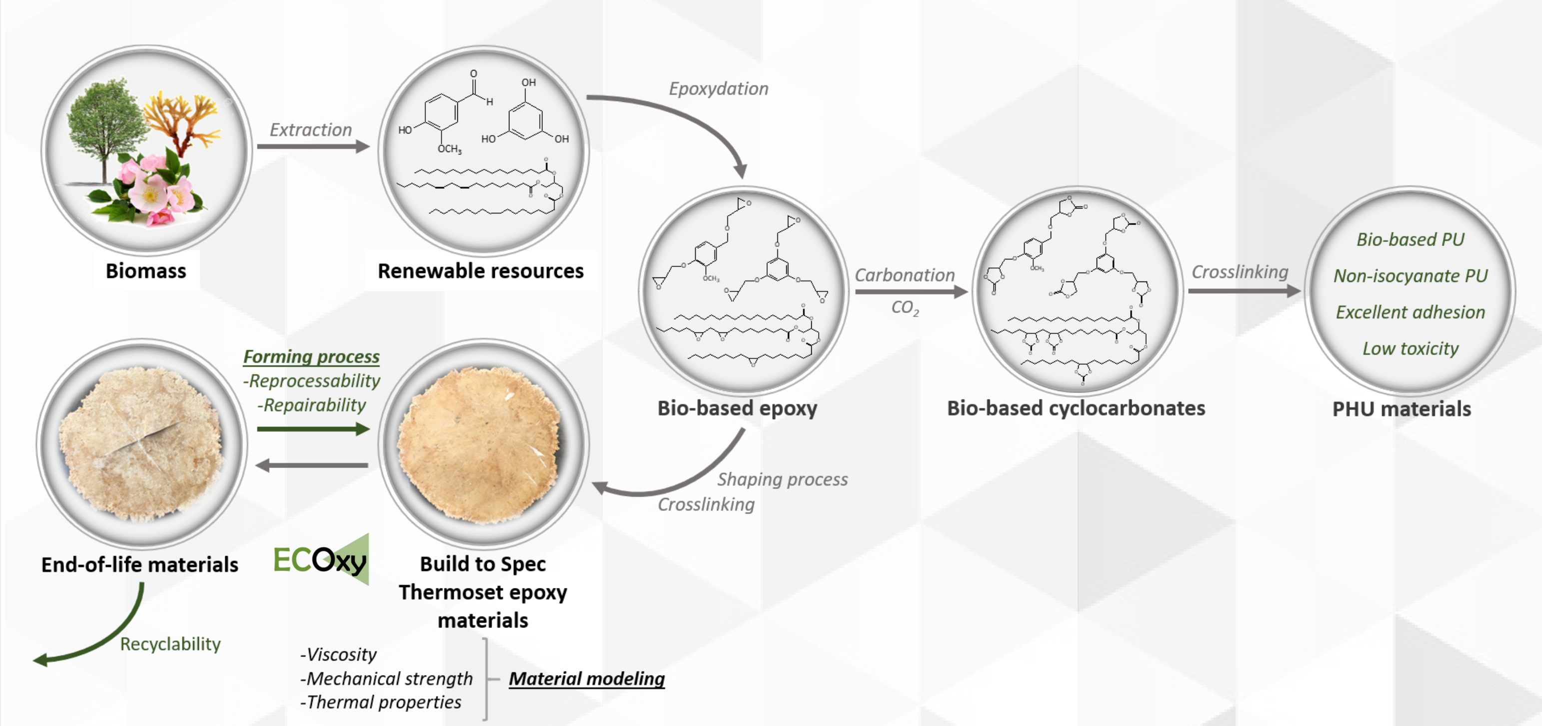
04 Sustainable Epoxy Resins

Introduction

Green material chemistry and biomass valorization is a fundamental aspect of SPECIFIC POLYMERS' research and development activities. Many industrial and collaborative projects are ongoing to find sustainable alternatives to fossil resources having an industrial viability. Indeed, our research efforts are mainly dedicated to (***Figure 1***):

(i) Sustainable building-blocks to substitute toxic and petro-based Diglycidyether of Bisphenol-A in epoxy resins
(ii) Cyclocarbonates for the synthesis of polyhydroxyurethanes to replace toxic isocyanate base polyurethane materials
(iii) Sustainable alternative building-blocks to substitute toxic phenol and formaldehyde in formophenolic resins
(iv) End-of-life phase of thermoset materials which own a lack of reprocessability, reparability & recyclability

Figure 1: SPECIFIC POLYMERS strategy for the development of thermoset materials



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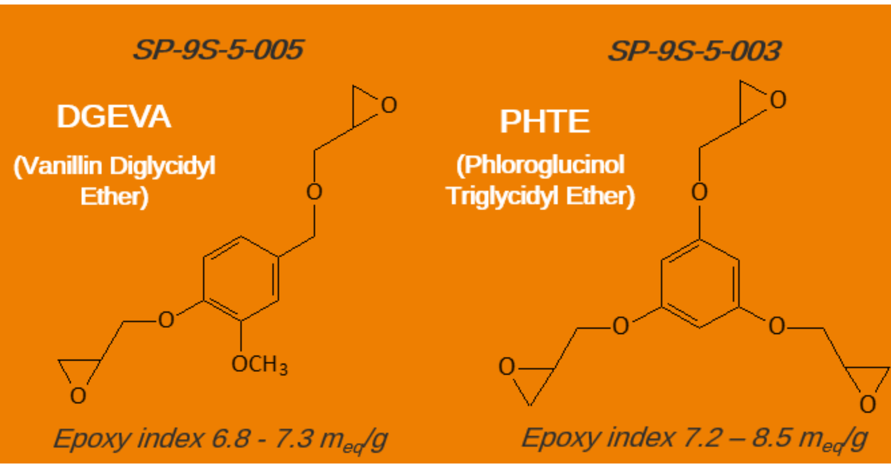
The research activity proposed by the company aimed at the development of innovative resins that fulfill all customer's specifications in terms of process and final properties (*i.e.* Build-to-Spec. resins). Development processes are mainly based on experimental researches but the company is moving toward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

Sustainable Building-Blocks to substitute DGEBA in Epoxy Resins

Among all R&D project of the company in the field of sustainable materials, a special attention will be given to sustainable epoxy building-blocks that can be used for the substitution of Diglycidylether of Bisphenol-A (DGEBA) into epoxy-amine materials. Alternative sustainable 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] (***Figure 2***). Both epoxy resins are aromatic multifunctional glycidyl ethers that can be combined to reach a range of thermomechanical properties.

Figure 2: Sustainable Aromatic Building-Blocks for Thermoset Epoxy resins



Both epoxy resins were evaluated and used in the preparation of epoxy-amine materials. Main objective here was to substitute the DGEBA used as epoxy resin in the reference material while retaining the same hardener for comparison purposes. The selection of the most promising resins was based on both processes' specification and final materials properties.

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

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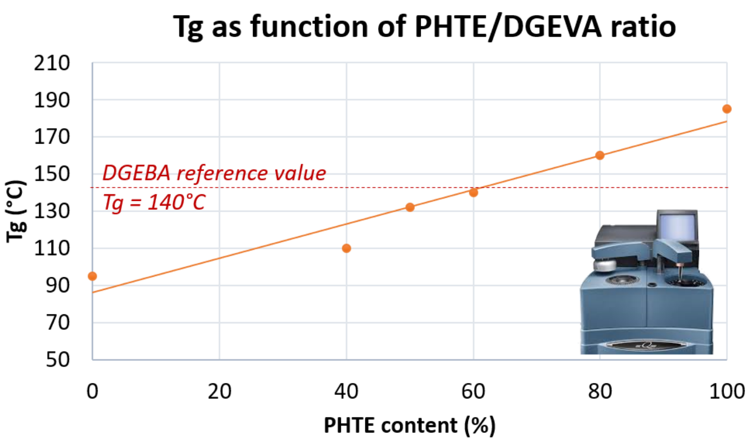
Both the viscosity and the glass transition temperature (Tg) of the cured resins were defined as the most representative parameters for the definition of the most promising resins to further developed for the applications of the project. Resins formulated on the basis of DGEVA and PHTE allow to reach Tg in between 90°C to 180°C while exhibiting viscosity consistent with the process (***Figure 3***).

Figure 3: Sustainable Aliphatic Building-Blocks for Thermoset Epoxy resins



	Process	Material
Key Performance Indicators	Mix Viscosity	Glass transition Temperature
Reference Resin DGEBA (5.1 m_{eq}/g ; 400 g/mol)	13 000 mPa.s	140°C
Biobased Resin PHTE/DGEVA 60/40 (%wt)	< 3845 mPa	140°C

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. Thus, from both these sustainable precursors, **it was possible to find a sustainable alternative to DGEBA in epoxy resin formulations**. It must also be noted that the mechanical performance of the final material can be tuned by varying the DGEVA/PHTE ratio if adjustments are needed while using other hardeners.

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 25 to 50 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.

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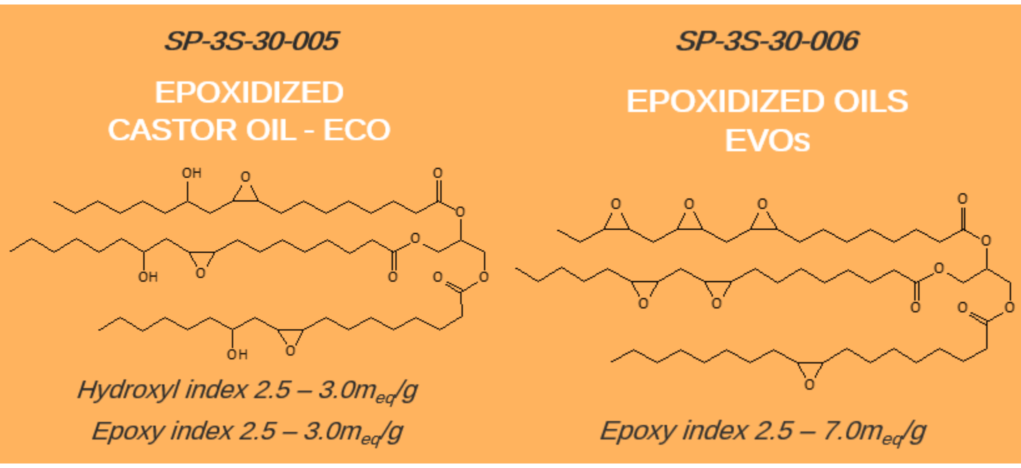
Bio-based Epoxy Resins – From Soft to Tough Materials

Working with DGEVA and PHTE allow reaching glass transition temperature in the range of 90°C to 180°C. Depending on the application, softer materials can be of interest and SPECIFIC POLYMERS is working for several years on the epoxidation of various vegetable oils (***Figure 4***). 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.

Figure 4: Bio-based Aliphatic Building-Blocks for Thermoset Epoxy resins



Thanks to vegetable oils diversity, the epoxy content of the EVOs supplied by SPECIFIC POLYMERS varies from 2.5meq/g to 7.0meq/g. Several experiments were set out to assess and compare the thermal and mechanical properties of both thermocured and photocured materials prepared from SP's EVOs leaflet. Finally, designed with biobased epoxy resins developed by SPECIFIC POLYMERS, materials exhibiting glass transition temperatures from -25°C to 180°C can be reached (***Figure 5***).

Figure 5: Tunable sustainable epoxy material properties: Selection of R&D products to reach soft to tough materials