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Biobased & Reprocessable Epoxy Resins

H2020 BBI-JU ECOxy Project

Nowadays, a significant part of **epoxy-based materials** worldwide is prepared from the **DiGlycidyl Ether of Bisphenol A (DGEBA)**. However, in Europe for several years now, there have been regulatory developments related to Bisphenol A (BPA) which has been classified as a **chemical of very high concern by the European Chemicals Agency (ECHA)** due to its toxicity.

[Read more >](#)

R&D of biobased and/or non-toxic precursors to substitute petro-based chemicals subjected to strong regulation is a significant aspect of SPECIFIC POLYMERS innovation activity. In this scope, SPECIFIC POLYMERS' research efforts are mainly dedicated to:

- (i) Biobased alternative building-blocks to substitute toxic and petro-based precursors (Bisphenol-A, Formophenolic, Isocyanates, etc.) in thermoset resins and composites and
- (ii) The end-of-life phase of thermoset materials that suffer from a lack of reprocessability, reparability and/or recyclability.

Within this research theme, **we strongly believe in ECOXY project** which aims to develop **innovative and sustainable biobased epoxy thermoset composites which exhibit reparability, reprocessability and recyclability** (Circular value chain).

[Learn more about the ECOXY Project >](#)

The ECOXY project involves complementary stakeholders and allows the sharing of skills and tools which led to genuine synergy to come up with innovative solutions. A consortium of 13 partners from 8 different European countries has been formed to meet the end-users

specifications. The value chain is made up of **synthesis and materials chemists (Resins & Fibres), manufacturers and industrial end-users.**

*This project has received funding from the **Bio Based Industries Joint Undertaking** under the **European Union's Horizon 2020** research and innovation programme under grant agreement No 744311. This article reflects only the consortium's view and that the JU is not responsible for any opinion.*

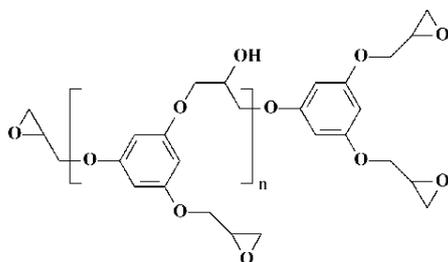


Within this project, SPECIFIC POLYMERS objectives were geared towards the development of innovative bio-based epoxy resins that can substitute DGEBA in the applications targeted by the project, *i.e.* in the automotive and construction sectors. Build-to-Spec. bio-based epoxy resins are being developed taking into account the specifications of both **the implementation processes used and end-users mechanical properties.** Two synthetic strategies were evaluated in parallel:

Aromatic Biobased Precursors: First strategy was to achieve the synthesis of aromatic resins bearing multi-functional glycidyl ether moieties. In this case, the study was based on the chemical modification of vanillin, vanillyl alcohol or phloroglucinol. Vanillin, Vanillyl alcohol can be extracted from Lignin^[1] and Phloroglucinol can be extracted from Algae^[2]. Both products were synthesized successfully in the scope of the project and are now sold for R&D purpose by SPECIFIC POLYMERS:

SP-9S-5-003 >

Phloroglucinol Triglycidyl Ether (PHTE)



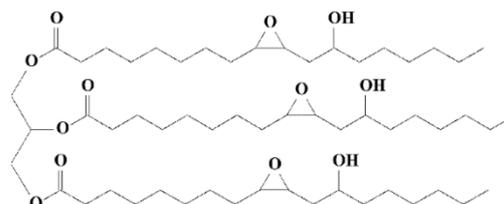
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Vanillin Alcohol DiGlycidyl Ether (DGEVA)

Epoxidation of vegetable oils: Second strategy concerns the epoxidation of unsaturated vegetable oils. A benchmark of available vegetable oils was achieved and the most interesting oils were deeply analyzed to determine their unsaturation content and adapt the epoxidation pathway. It was finally possible to synthesize a wide range of epoxidized vegetable oils exhibiting an epoxy content from 2.5 meq/g to 7.0 meq/g. These epoxidized oils are now commercialized by SPECIFIC POLYMERS for R&D purpose.

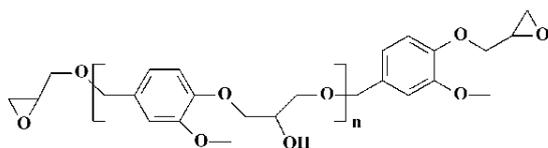
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Corresponds to epoxidized castor oil and differs from the other oils because of the hydroxyl groups in β -position to the epoxy rings.



SP-3S-30-006 >

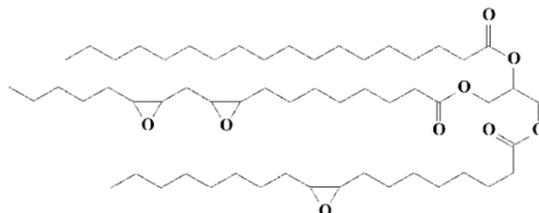
Corresponds to epoxidized vegetable oils of similar chemical structure but varying from their content of



[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 >

epoxy functions. They are obtained from various vegetable oils such as Saint John's Wort oil or Rapeseed oil for instance. As much as possible, non-edible oils were favored in the selection of the vegetable oil precursors.



All these epoxy resins were evaluated and used in the preparation of epoxy materials with hardeners of different nature. **DGEVA and PHTE was retained as the most promising materials for ECOXY project.** An in-depth development work was achieved to enhance the synthetic protocols of both these epoxy precursors and SPECIFIC POLYMERS is now working in close collaboration with its toll-manufacturer to scale up the production of these resins from 25 kg to 50kg by the end of 2019. Moreover, The 3R functionalities are achieved by combining aforementioned SP bio-based epoxy building-blocks with suitable dynamic hardeners^[3]. Compatibilization with flax fibers or PLA fibers is currently being studied to prepare corresponding 3R composite materials.

[3] 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 >

[See corresponding article on Ecoxy website >](#)

Maleimides containing polymers are gaining a great deal of attention in both scientific and industrial communities since they can be used in high performance macromolecular systems such as **self-healing materials, biological materials, high temperature thermosets materials or UV-curable materials.**

[Learn more about maleimides: Newsletter october 2018 >](#)

Publication of the Month

[The influence of Stereochemistry on the Reactivity of the Diels - Alder cycloaddition and the implications for reversible network polymerization >](#)



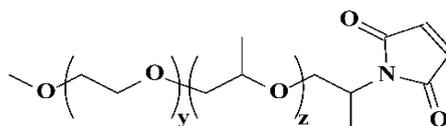
Authors: A. Cuvellier, R. Verhelle, J. Brancart, B. Vanderborght, G. Van Assche and H. Rahier
Focusing on self-healing properties, A. Cuvellier and coworkers published a very interesting article (Polymer Chemistry, August 2018) explaining the influence of the stereochemistry of furan-maleimide Diels–Alder reaction on the kinetics of the reversible network formation in the absence of solvents. In this work, poly(propylene oxide) bismaleimide from SPECIFIC POLYMERS ([SP-1P-9-017 >](#)) was evaluated within this study.

[More Publications >](#)

Product of the Month

[PEO PPO Maleimide – SP-1P-9-016 >](#)

In the same research area, SP wants to highlight this month SP-1P-9-016 reference that correspond to poly(ethylene oxide-co-propylene oxide) bismaleimide.



[More Functional Polyethers >](#)

News & Events

SPECIFIC POLYMERS is engaged in the development of new innovative solutions and had the opportunity to take part in various events promoting **bio-sourced innovations**. In 2018, we participated to the **N.I.C.E 2018 Conference** (Nature Inspires Creativity Engineers) which brought together hundreds of scientists and engineers to share the latest developments in the growing field of bioinspired and bio-based chemistry and materials.

In addition, this year SPECIFIC POLYMERS participated in **Polyray 2019** which focus on the cationic photopolymerization of bio-based epoxy monomers and we gave a presentation

Collaborative Project

SPECIFIC POLYMERS is involved in the development of bio-sourced composites for the aeronautical sector as part of the **BAMCO project** (Bamboo long fibre reinforced bio-based Matrix Composite). SPECIFIC POLYMERS role within this project is to realise the **formulation and the implementation** of the biobased polymers constituting the composite matrices.

The main objective of such a project is to replace in aircraft design and manufacturing the most **common composites which can be heavy and toxic by bamboo fibre/biobased resins composites**. Bamboo owns good thermal resistance and is 2.5

at the **IAR in Montpellier** about SPECIFIC POLYMERS' overall strategy regarding the development of future bio-based materials.

times less dense than glass with equivalent mechanical module.

[N.I.C.E 2018 >](#)
[Polyray 2019 >](#)
[IAR Presentation >](#)

[BAMCO Project >](#)

Collaborative Projects

For more than 15 years, SPECIFIC POLYMERS (SP) is involved in collaborative projects whether at the **National** (ANR, FUI, FEDER, etc.) or **European level** (FP6, FP7, H2020 – BBI-JU, CLEAN SKY, etc.). The involvement of the company has grown over time. Depending on the project, our role can be either simple participant, Task-leader or WP-leader. Recently, our team had also experienced the setting up of a project as technical manager. In the future and for the most strategic projects, we are willing to increase our involvement and participate more actively in **consortium building, project definition and project set-up**.

We are convinced that our **transversal skills and competences in material innovation** topics can be an added value in many projects. Within this framework, SP wishes to implicate more its large network made up of partners, suppliers and customers. SP has interest in **RIA and IA projects** since our activity extends through pure R&D activity and low TRL to the support toward scaling-up and first industrialization steps of most promising products. Such projects are opportunities for us to go further in our strategic research subjects like **high performance batteries (LC-BAT calls), sustainable materials (BBI-calls) or high-performance composites and coatings (JTI-CS2 calls)** for instance.

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