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Biomass-derived Phenylpropenes as Precursors of Thermosetting Epoxy Resins: From Synthesis to Materials

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As demonstrated by the current international awareness, and supported by several independent studies, the replacement of fossil fuels and the need to find competitive alternatives are crucial issues to reduce global warming, and to limit the consequences for life on Earth [1]. As part of this challenge, the biomass and molecules from the living can be considered as providential pools of renewable building blocks dedicated to the chemistry of the future. This is particularly true in polymer science, where the use of renewable resources for the synthesis of fully or partially biobased materials arouses a great deal of interest, in academia and industry [2].

In the epoxy thermosets field, more than 90% of formulations are made from bisphenol A diglycidylether (BADGE) [3]. However, bisphenol A is seriously suspected to be an endocrine disruptor for animals and humans, and moreover exclusively synthesised from phenol. With the objective to find alternatives to BADGE-based resins, our team has recently shown the possibility to use a bio-based diepoxide monomer, named glycidylether epoxyde of iso-eugenol (GEEp iE, Fig 1), prepared from iso-eugenol which can be catalytically extracted from lignin [4].

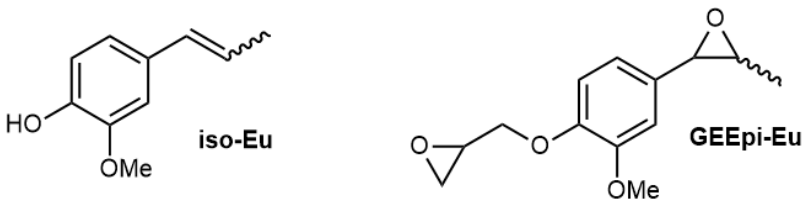

Figure 1. Iso-eugenol and GEEpi-Eu chemical structure

Thus, this monomer is easily cross linked in the presence of acid anhydrides leading to thermoset materials which in certain cases (camphoric, phthalic, diphenic anhydride) exhibit glass transition temperatures above 100 °C [5]. Nevertheless, the synthesis of GEEp-iEu requires two steps involving in particular a purification by column chromatography on silica gel during the first stage. Thus, this step limits its development, both from an industrial and ecological points of view. In order to improve the synthesis of GEEp-iEu and to consider its future scale-up, we focused more specifically on the identification of the co-products, and on their potential valorization. Thus, two additional compounds, **B** and **C** respectively, have been identified and fully characterized (by infrared and multinuclear NMR spectroscopy, mass

spectrometry, and elemental analysis). Interestingly, both retain propenyl groups, which can also be oxidized to lead to diepoxy derivatives (**BEp** and **CEp**, Fig. 2).

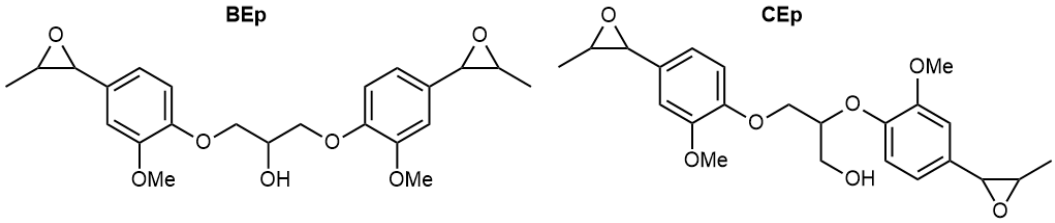

Figure 2. BEp and CEp chemical structure

These epoxy monomers were then engaged in curing reactions, separately and together with GEEp iE, in the presence of anhydride (which can be also biobased [6]). High glass transition temperatures (120°C to 160°C) were measured for the different cross-linked polymers obtained. First mechanical and rheological studies indicate similar properties as those obtained with epoxy material derived from BADGE. In addition to the green chemistry approach applied to the monomers synthesis, these results will be detailed during the presentation and compared to traditional epoxy material obtained from BADGE.

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