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## BIOPOL-2019 ABSTRACT

### DESIGN OF AN EPOXY PREPOLYMER BASED ON CHESTNUT AGRO-RESIDUES

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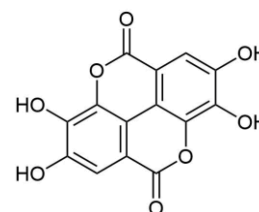
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For centuries, chestnut is a major crop of the C  vennes region in the south of France [1]. However, in these days, the exploitation of chestnut trees is drastically declining because of local strategies and diseases (cynips). Therefore, it becomes strategic to explore chestnut valorization alternatives than existing ones, i.e. energy and agriculture, in order to renew C  vennes forests and to develop a new economic activity in the region.

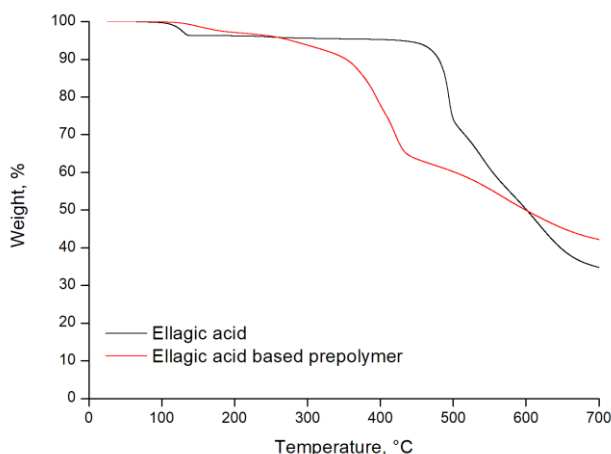
According to literature, chestnut wood is greatly rich in hydrolysable tannins [2,3]. Ellagic acid (**Figure 1**), a dilactone of hexahydroxydiphenic acid (HHDP), is encountered in chestnut extracts [4]. This chemical can be obtained in higher amounts after hydrolysis of chestnut extracts or plant materials. Due to its aromatic nature and high thermal stability (**Figure 2**), ellagic acid displays an important interest for the synthesis of biobased prepolymers for epoxy resins.

Therefore, the main objective of this study is to find a way to convert ellagic acid into the corresponding epoxy prepolymer for the formulation of biobased heat – resisting epoxy resins. In this work, the functionalization of ellagic acid was carried out using a two – step synthesis involving the allylation of OH groups followed by the epoxidation of resulting double bonds (**Figure 3**). This chemical modification method is well known and has already been applied to natural polyphenols [5].

The first functionalization step – allylation, – consisted in the substitution of hydrogen atoms of ellagic acid hydroxyl functions by allyl groups (**Figure 3**). A chaotropic salt was initially added to the methanolic solution of ellagic acid in order to favour a better dissolution of the phenolic compound in the solvent. The reaction of ellagic acid with 16 molar eq of allyl bromide and 4 molar eq of potassium carbonate during 7 days at 35  C allowed the full conversion of ellagic acid into allyl derivatives. The raw product was recovered as a cream – coloured powder by filtration (76% yield). UPLC – DAD – MS and NMR analyses essentially showed the formation of tri – and tetra – allylated derivatives of ellagic acid.



**Figure 1** - Chemical structure of ellagic acid



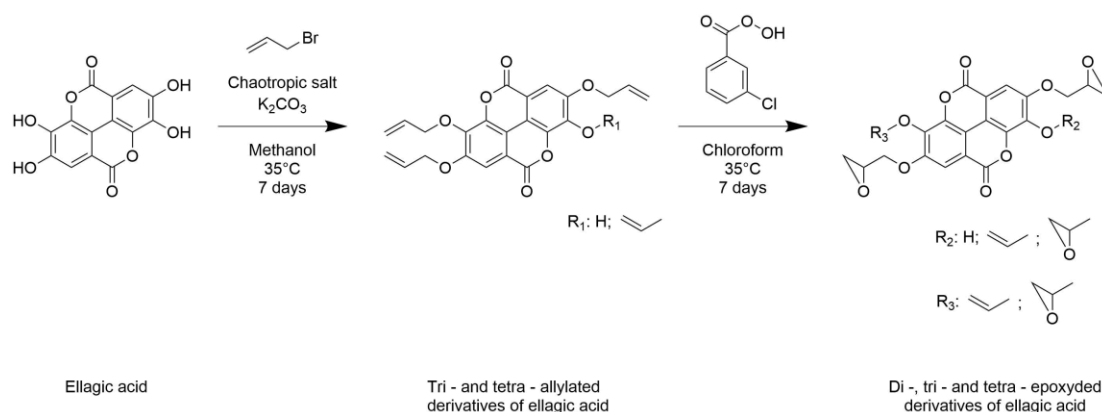
**Figure 2** - Thermograms of ellagic acid and ellagic acid based prepolymer under nitrogen flow

The second step is an epoxidation of the double bonds of the allyl groups of the derivatives (**Figure 3**). For that, the raw product (containing tri- and tetra-allyl derivatives) was reacted with 4 molar eq of *m*-chloroperbenzoic acid (*m*-CPBA) in chloroform during 7 days at 35°C. The final product was recovered by liquid-liquid extraction and then vacuum concentrated to dryness. The final product was a cream-coloured powder (65% yield). UPLC-DAD-MS analysis indicated the formation of di-, tri- and tetra-functional epoxy monomers.

Some characteristics of the prepolymer, necessary for the formulation with the hardener and the curing, were subsequently evaluated in the present work. The epoxy equivalent weight (EEW) was determined according to the protocol of Aouf [6]. The mean EEW value of the epoxy prepolymer was estimated at 169 g/eq epoxy and corresponded to the expected value. The degradation temperature of the epoxy prepolymer, measured by a TGA analysis under nitrogen flow, was estimated to be 396°C (**Figure 2**). Therefore, the incorporation of epoxy functions in the structure of ellagic acid induces the reduction of its thermal stability. However, the thermal characteristic of the biobased prepolymer is still important.

The results evidenced the possibility to synthesize an epoxy prepolymer from ellagic acid. In view of its important thermal stability, the prepolymer will be then employed for the formulation of biobased heat-resisting epoxy resins. The thermo-mechanical properties of the biobased epoxy resins will be carried out as well.

The same synthesis will next be applied directly on chestnut raw extracts and the performance of the corresponding resin will be compared with both the ellagic acid- and DGEBA-based resins. The evaluation will rely on the results of TGA, DSC, DMA and PCFC analyses of the formulated epoxy resins.



**Figure 3** - Synthesis of epoxy prepolymer based on ellagic acid

## References:

- [1] Institut National de l'Information géographique et Forestière. Résultats d'inventaire forestier. 2013, 57.
- [2] R. Garcia, B. Soares, C.B. Dias, A.M.C. Freitas, M.J. Cabrita. Eur. Food Res. Technol. 2012, 235, pp 457–467.
- [3] S. Eichhorn, S. Erfut, T. Hofmann, S. Seegmuller, R. Nemeth. 2017, 62, pp 181–196.
- [4] M. Sanz, E. Cadahia, E. Esteruelas, A.M. Munoz, B. Fernandez De Simon, T. Hernandez, I. Estrella, J. Agric. Food Chem. 2010, 58, pp 9631–9640.
- [5] C. Aouf, H. Nouailhas, M. Fache, S. Caillol, B. Boutevin, H. Fulcrand. Eur. Polym. J. 2013, 49, pp 1185–1195.
- [6] C. Aouf, S. Benyahya, A. Esnouf, S. Caillol, B. Boutevin, H. Fulcrand. Eur. Polym. J. 2014, 55, pp 186–198.