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Elaboration de résines époxy à partir de phénols naturels

From natural phenols to biobased epoxy resins

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Thermosetting polymers represent between 15 and 20% (volume) of the total polymer market [1]. Among the different types of thermosetting polymers, epoxy resins account for almost 70% of the market, with an annual production of around 4 Mt [2]. Global epoxy resin market was around USD 21.5 billion in 2016 and it was estimated to reach USD 27.5 billion in 2020 and reach USD 37.3 billion in 2025[3]. The success of this type of resin is due to the excellent mechanical resistance of these materials (shear strengths between 5 to 30 MPa), as well as its high resistance to chemicals, humidity and corrosion. These resins are composed of monomers or prepolymers which generally have at least two epoxy functions. Over 90% of commercial epoxy resin formulations use bisphenol A diglycidyl ether (DGEBA or BADGE). DGEBA is a particularly interesting reagent for the synthesis of epoxy resins, since it gives remarkable properties to crosslinked materials. The epoxide functions present in the ends of the DGEBA (glycidyl ether functions) are quite reactive functions, which reduce the temperature and/or the crosslinking time compared to other types of epoxide functions. On the other hand, the presence of aromatic rings significantly improves the thermal properties. However, DGEBA is synthesized from bisphenol A (BPA) and epichlorohydrin (ECH). BPA production was around 6 million tons in 2017 and the growth rate is expected to be 6% per year for the period 2019-2024. About 66% of the BPA produced is used in epoxy resins, which is the main industry using this compound. However, BPA is a substance that has been classified as reprotoxic 1B by the European Chemicals Agency (ECHA). Additionally, this substance is an endocrine disruptor that can mimic the body's hormones and lead to deleterious health effects, even at very low doses [4]. Moreover, since March 2018, the REACH regulation has severely restricted its use for products intended for consumers. For example, thermal paper containing more than 0.02% BPA cannot be marketed in the EU since January 2020.

Vanillin is an aromatic aldehyde with a phenolic hydroxyl group. It is the molecule that gives the characteristic aroma to vanilla. This molecule can be extracted directly from the vanilla pod, but it can also be obtained by synthesis from petro-sourced precursors or from lignin. It has an aromatic ring with a phenolic hydroxyl group and an aldehyde. These reactive functional groups allow the functionalization of vanillin to obtain epoxide monomers. Vanillin can be easily transformed into vanillic acid, vanillic alcohol and 2-methoxyhydroquinone. These three molecules can react directly with ECH to produce the three di-epoxy monomers with glycidyl ether functions (Figure 1) which can be used to prepare bio-based epoxy resins[5, 6]. In this case, the three epoxy resins were cured with isophorone diamine (IPDA) at 100°C for 1 h, then at 125°C for 1.5 h and finally at 160°C for 1 h. The thermomechanical properties of these polymers were then compared to those obtained with DGEBA/IPDA, obtaining quite similar results (T_g, modulus of elasticity, thermal stability and crosslinking density), in particular for di-vanillic acid. epoxide which has excellent thermomechanical

properties. Moreover, given that these monomers have epoxy functions of the glycidyl ether type, the crosslinking reaction can in principle take place at ambient temperature. The biobased carbon content will depend on the vanillin derivative and whether or not the biobased nature of the ECH used for the O-glycidylation reaction (54-100% biobased carbons).

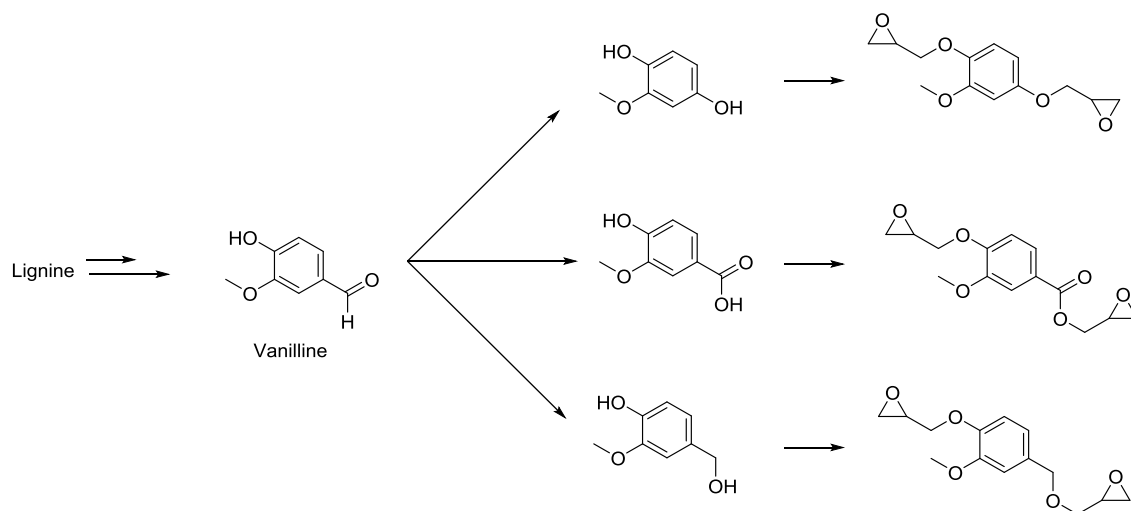


Figure 1: Synthesis of lignin-based epoxidized vanillin derivatives

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