Utilization of pulp and paper industry waste (Kraft lignin) for the production of bio-based epoxy composites

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Lignin is one of the three main structural components of lignocellulosic biomass, representing the most abundant natural source of aromatics and phenolics. Lignosulfonates, Kraft lignin and other related types of lignins are recovered in huge amounts (Mtons/year) as side products in the pulp and paper industry. However, they are highly underutilized in the currently available biorefinery schemes as they are traditionally used for the in-house production of heat and energy (Constant *et al.*, 2016). Lignins' macromolecule consists of phenylpropanoid monomers, namely, coniferyl (G units), sinapyl (S units), and p-coumaryl (H units) alcohols with various functional groups such as hydroxyl, carbonyl, methoxy and carboxyl groups. Thus, due to its highly aromatic/phenolic nature and hydroxylated surface, lignin has attracted a lot of scientific and industrial interest in the last decades, in a majority of fields like energy, fuels, chemicals and especially in the polymer science field, aiming at its utilization towards the production of new bio-based polymers and composites.

Thermoset and thermoplastic polymers like epoxy and phenol-formaldehyde resins, PLA and PUs, have been studied as potential substrates for addition of said lignins (Cui *et al.*, 2013). Due to its substantially/highly versatile structure lignin can be used as isolated (without further modification) or after various treatments, e.g., mechanical or chemical modifications (glycidylation, phenolation, amination etc.) or by using solvent fractionation, in order to further enhance reactivity and chemical affinity with the polymers (Laurichesse *et al.*, 2013). One of the most commonly used thermosetting polymer, the epoxy resins, have attracted a lot of interest the past years due to their high thermal and chemical resistance and their superior mechanical properties. Nevertheless, epoxy resins are produced by the reaction of petroleum-based and highly toxic bisphenol-A (BPA) and epichlorohydrin that yield diglycidyl ether of bisphenol A (DGEBA), which is a non-recyclable, fossil dependent chemical (Nikafshar *et al.*, 2017). Therefore, there is an increased interest in further exploiting the use of technical lignins and especially of Kraft lignin, since it is an underutilized waste product of the pulp and paper industry, towards the production of green and bio-based epoxy composites.

In this work, Kraft lignin was utilized towards the production of lignin-based epoxy composites, as presented in Figure 1. Kraft lignin was used either as received or after chemical or mechanical treatment/fractionation that included solvent fractionation, glycidylation and ball milling. The fractionation of kraft lignin in ethanol resulted in separation of nano-lignin while its functionalization with epoxy rings (glycidylation) was achieved via reaction with epichlorohydrin in a methanolic sodium hydroxide (NaOH) solution at 80°C. Ball milling was performed for 2 and 8 h. Structural and morphological characteristics of initial and treated lignins were investigated using FT-IR, GPC, NMR, TGA etc. Initial kraft lignin was tested as a curing agent and as a filler/additive in the lignin/epoxy composites using commercially available epoxy resin, i.e., diglycidyl ether of bisphenol A (DGEBA) and Jeffamines D-230 (glassy system) and D-2000 (rubbery system) as curing agents when needed. Chemically and mechanically treated kraft lignins were also studied as fillers/additives in the epoxy composites. The composites were prepared by in-situ polymerization, followed by curing at selected conditions.

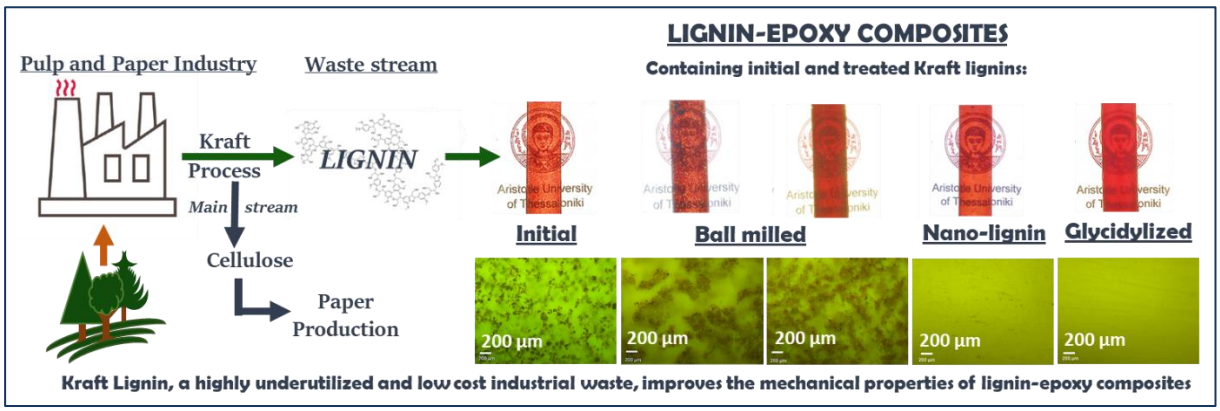

Figure 1. Utilization of Kraft lignin, a pulp and paper industry waste, in bio-based epoxy polymer composites

The mechanical properties of the prepared composites were tested using tensile test measurements. The utilization of Kraft lignin as curing agent was successful in both glassy and rubbery epoxy composite systems. In more detail, improved stress and stiffness were achieved for up to 5 % replacement of commercial curing agent by Kraft lignin in the glassy epoxy system. Interestingly, up to a 34% replacement was achieved with the rubbery epoxy composites that also exhibited an improvement of stress, stiffness and strain before break. The glassy epoxy composites containing initial kraft lignin and all treated lignins (nano-, ball milled- and glycidylized lignins) as fillers exhibited increased strength and stiffness at low loadings (3 wt.%) and gradual deterioration of mechanical properties at higher contents. In the rubbery lignin/epoxy composites containing initial and treated kraft lignins, a substantial increase in the mechanical properties was achieved at low lignin loadings (3 wt.%), while increase of lignin loading resulted in further improvement in strength, elongation and stiffness.

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