Safety and Sustainability Challenges Facing Phenolic Resins: Advances and Substitutions

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The synthesis of the phenolic resin was discovered by Baekeland a century ago adhesive and their excellent environmental resistance, adhesive capabilities, and fire high performances make them ones of the main wood adhesives but also in automobile, aerospace, composite materials, and other sectors. Phenolic resins are still widely used today with a global production of about 12 million tons/year. Usually, these resins contain residual free formaldehyde, which is highly toxic and carcinogenic and will soon be banned by the the REACh regulation. Consequently, phenolic resins must be revisited and/or substituted. Commonly, urea is added to phenolic resins as formaldehyde scavenger but urea is not relevant for high-temperature applications. Thus, an easy-to-implement method was developed with an aminophenol, giving access to a noncarcinogenic resin while maintaining the thermomechanical properties. The chemistry and the reaction mechanism of aminophenols with formaldehyde is described. The interest of this additive is multiple 1/ for trapping of formaldehyde to fit the REACh regulation, *i.e.* < 0.1 wt. %free formaldehyde) and 2/ maintaining the thermostability of the modified phenolic network (Td5% = 395 °C and char yield = 63%). This method which is applicable on an industrial scale, uses mild reaction conditions and limits volatile organic compound emissions, *i.e.* two ways to improve durability and reduce toxicity of the resin.

The other route investigated is the design of "phenolic"-like resins without phenol or formaldehyde by substitution with "simple" molecules. The substitution of formaldehyde with aromatic aldehydes is a relevant way to ensure that the cured resin has degradation properties comparable to phenol/formaldehyde resins. In particular, terephthalaldehyde (TPA) appeared to be the most relevant candidate leading to thermostability properties similar to conventional phenolic resins but have too poor mechanical properties to be used as matrices in composite materials. The substitution of phenol with other phenolic compounds (including biosourced ones) was considered in order to increase the mechanical properties of the cured resin, but also to limit the toxicity of the unreacted liquid resins. Several compounds such as hydroxymethylphenols (HMP), resorcinol, 3-methoxyphenol, orcinol, 3-methylcatechol, hydroquinone, phloroglucinol, or 3,5-dimethoxyphenol were considered. All the results showed that the substitution of the phenol by a non-functionalized phenolic compound decreased the degradation behavior, except resorcinol, and did not afford materials with acceptable mechanical properties. Nevertheless, 2-HMP and 4-HMP (incl. without an alkali base), allow for obtaining materials with very interesting thermostability and thermomechanical properties. In addition, 2-HMP and TPA are non-toxic and the synthesis of this type of resin would be easily scalable. These compounds could be sustainable, 2-HMP could be produced by the reduction of salicylaldehyde (bio-renewable resource from lignin), and TPA could be produced by the reduction of terephthalic acid (potentially biosourced). Thus, these types of resins would be suitable candidates to replace conventional phenolic resins.

Keywords: phenolic resin, polyaddition, formaldehyde-free, biobased

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