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Synthesis of bio-based amine monomers for epoxy curing

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PURPOSE OF THE ABSTRACT

Nowadays, epoxy thermosets are widely used in various applications such as paints, coating, and composites. Because of their high thermo-mechanical properties and chemical resistance conferred by their aromatic moieties from epoxy reagent, thermosets are invaluable in industry. However, they are cross-linked polymers and thus cannot be recycled. Consequently, in the order to decrease the carbon footprint, the recent interest in the use of renewable raw materials to prepare thermosetting polymers is increasing and the number of contributions to this subject is growing rapidly.

Currently, most of the worldwide epoxy polymers are derived from diglycidyl ether of bisphenol A (DGEBA) which confers aromatic moieties inducing excellent thermal and mechanical properties to the epoxy thermosets. However, DGEBA is petroleum-based and derived from bis(4-hydroxyphenylene)-2,2-propane (bisphenol A, BPA), a recognized endocrine disruptor which can have important consequences on the human health. Consequently, many studies recently led to new bio-based or less toxic BPA and DGEBA substituents. Nevertheless, these renewable resources generally led to poorer networks properties than those of DGEBA-based networks, due to the absence of aromatic groups.

Another way to bring aromaticity to the final network is the amine structure. In fact, epoxy networks are cross-linked systems which can be obtained by the reaction between a diepoxy prepolymer and a diamine hardener. However, aromatic amines are often dangerous and often have low reactivity. Moreover, most of the current amines are issued from petrochemical resources and only a few amines are derived from biomass (chitosan and Lysine). In addition to natural amines, only a few synthetic pathways exist for obtaining bio-based amines by chemical functionalization of molecules originating from biomass (such as polyols, terpenes, lignin and vegetable oil). Furthermore, these syntheses can require some toxic reactants which are not appropriate within an environmentally friendly context.

Bio-based amines containing aromatic groups could be a solution to provide aromatic moieties to the final epoxy network conferring high thermo-mechanical properties and chemical resistance. Moreover, access to bio-based and non-harmful aromatic amine monomers is one of the main industrial challenges over the coming years.

In this context, we aimed at developing a simple and inexpensive method to synthesize amines, in accordance with green chemistry principles. In our work, easy and cheap method to achieve primary amines is targeted, i.e. by direct bio-based epoxide group amination with inexpensive nucleophile in presence of 2-methyltetrahydrofuran, a ?green? alternative ether solvent compare to dioxane. To reach new bio-based diamines, we tried to take advantage of new recently developed monomers to substitute DGEBA. To this end, we have decided to promote DGEVA, a previous epoxy derivatives from biomass developed in the laboratory. Then, these newly formed amines were added to epoxies to form thermosets by cross-linking. After curing, the thermal and mechanical behaviors of the synthesized networks were determined and compared to a petroleum-based reference system with DGEBA as epoxy. With this methodology, the chemical industry would only need one reactant and aqueous ammonia to obtain bio-based epoxy networks.

FIGURES

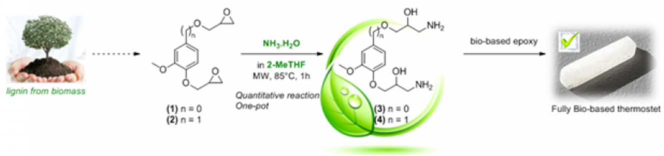

FIGURE 1

Figure 1

Bio route to DHAVA

FIGURE 2

KEYWORDS

bio-based | thermosets | vanillin | amine

BIBLIOGRAPHY