



Biobased epoxy thermosets from vanillin-derived oligomers



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ABSTRACT

Novel vanillin-derived epoxy oligomers were prepared and crosslinked to yield biobased epoxy thermosets. This work directly continues the efforts engaged by our team to use vanillin as a renewable building block for polymer chemistry as it is an industrially available, non-toxic, wood-derived compound. The oligomers were synthesized by adapting and optimizing an industrial strategy currently in use, consisting in the chain-extension of a diepoxy monomer in excess by the poly(addition) of a diphenol. The length of the oligomers prepared was controlled by the stoichiometry of the reactants, and well-predicted by Carothers' equation. A ^1H NMR titration method was implemented to determine the epoxide indexes of the oligomers, which were very close to the ones calculated. The thermal properties of the oligomers were investigated and their T_g increased with the chain length, in accordance with the Flory–Fox equation. Thermosets were prepared by crosslinking these biobased epoxy oligomers with a common industrial amine hardener. The materials obtained displayed good thermo-mechanical properties that were tunable with the chain length of the oligomer employed. The current strategy used in industry was found to be applicable to renewable resources-based epoxy resins.

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1. Introduction

In a context of environmental concerns and predicted scarcity of petrobased resources, the use of renewable resources is an ecological and economical necessity. The polymer industry has its role to play in this transition and the biosourcing of polymers is currently a hot topic for both academic and industrial research in this field.

Great efforts have been made toward this goal during the last decade [1]. These efforts were successful in some areas like the development of polymers based on plant oils [2], which is already an industrial reality. The field of (poly)saccharides is also currently under intense investigation [1], either for a direct use like cellulose or starch, or indirectly to prepare from this resource all-purpose building-blocks [3]. This approach led to the development

around these building-blocks of platforms of monomers and compounds usable in polymer chemistry like in the case of isosorbide for instance [4].

However, aliphatic monomers give polymers with low T_g – especially long fatty acids from plant oils – which is not suitable for applications with demanding thermo-mechanical properties. Also, polymers from poly(saccharides) have a tendency to take up water, which might also limit the potential applications. Thus, the development of a sourcing of aromatic intermediates from renewable resources is a key challenge, especially since the petro-based raw materials tend to shift from oil to shale gas, which limits aromatic availability. This is especially true for thermosetting materials as the presence of aromatic rings, very stable moieties, brings the thermo-mechanical performances required for this kind of polymers in their industrial applications. Moreover, thermosetting materials, being cross-linked, cannot be recycled and thus need a renewable carbon content as high as possible. Regarding

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the importance of this topic, the past few years have seen an increasing contribution from the scientific community, mostly at the academic level [5].

Epoxy polymers especially have been investigated [6] as they are used in many industrial fields such as aerospace, automotive and construction and through diverse applications such as adhesives, coatings and composite matrices. Currently, 75% of the epoxy polymers worldwide are based on Bisphenol A, a reprotoxic compound [7] that is under close monitoring and the use of which might be restricted in certain applications in the future. The use of renewable aromatics to prepare new, biobased epoxy polymers could thus have the double positive effect of Bisphenol A replacement and renewable resources use.

As mentioned, research and process development for the use of renewable aromatics are only at the starting point in this area, and epoxy thermosets are no exception. The only biobased epoxy prepolymers industrially available are based on cardanol. However, this abundant biobased phenol extracted from the cashew nutshell present a C₁₅ aliphatic chain, which decreases the thermo-mechanical properties of the final material [8]. Recently, a handful of reports could be found in the literature on the subject of biobased aromatics for high-performance epoxy polymers. Some authors started directly from the raw resources such as lignin [9,10] or tannins [11,12]. This approach, however, suffers from several drawbacks such as structure complexity of the resource, issues with processability due to reactivity, high molecular weights and insolubility and composition variability depending on the species or the time of year.

Another strategy found in the literature consists in synthesizing aromatic epoxy monomers from various biobased aromatic molecules such as furans [13,14], 4-hydroxybenzoic acid [15], cinnamic acid [16], catechin [11,17], gallic acid [18], eugenol [19], vanillic acid [20] and vanillin [21–23]. Among them, vanillin and derivatives are especially interesting as vanillin is the only monoaromatic compound currently industrially produced from lignin [24]. In a previous paper [25], our team investigated the functionalization of vanillin and its derivatives at different oxidation states. These molecules formed a platform of potential biobased difunctional monomers, including epoxy monomers. Biobased thermosets were then synthesized from these vanillin-derived aromatic epoxy monomers [26]. The epoxy materials prepared exhibited excellent thermo-mechanical properties; however they were only based on monomeric units. Usually, industrial epoxy resins are not purely monomeric but oligomeric. This strategy holds numerous advantages such as control of the properties through the degree of polymerization of the oligomer used or an easier handling by avoiding crystallinity of pure monomers [27].

In this study, we decided to go one step further and apply this established industrial method to biobased epoxy thermosets. The strategy of this work is summed up in Scheme 1. This strategy necessitated the syntheses of methoxyhydroquinone **2** and diglycidyl ether of methoxyhydroquinone **3** from vanillin **1**. These syntheses were previously described by our team [25]. We then adapted and optimized an industrial method to obtain

oligomers **4** from the reaction between **2** and **3**. With this method, oligomers with varying degrees of polymerization were prepared. We also developed a ¹H NMR titration protocol to measure the epoxide index of these oligomers. Finally, they were cross-linked with isophorone diamine, a common industrial hardener, to obtain vanillin-based thermosetting polymers with tunable properties.

2. Experimental

2.1. Materials and methods

TriEthylBenzylAmmonium Chloride (TEBAC) (99%), triphenylbutylphosphonium bromide (99%), methoxyhydroquinone (>98%), IsoPhoroneDiAmine (IPDA) (>99%), sodium hydroxide (>98%), 1,3,5-trioxane (>99%), trifluoroacetic acid (99%) and all solvents used (>99%) were purchased from Sigma–Aldrich. Epichlorohydrin (>99%) was purchased from Fluka. All reactants were used as received.

Silica gel chromatography was performed on a Grace Davison Reveleris Flash Chromatography device.

MS measurement was performed on a Waters Synapt G2-S High Resolution Mass Spectrometer (HRMS) equipped with an electrospray ionization source.

2.2. Synthesis of diglycidyl ether of methoxyhydroquinone **3**

A round-bottomed flask was filled with methoxyhydroquinone (**2**, 1.0 eq.), TEBAC (0.1 eq.) and epichlorohydrin (10 eq.). The mixture was stirred for 1 h and a half after reaching 80 °C and was then cooled down to room temperature. An aqueous solution of TEBAC (0.1 eq.) and NaOH (4 eq., 5 mol L⁻¹) was then added and the mixture was stirred 30 min at room temperature. Ethyl acetate and deionized water were added and the two-phase mixture was stirred for a few minutes. The aqueous phase was extracted three times with ethyl acetate. Organic phases were combined, rinsed twice with brine, dried on anhydrous MgSO₄ and filtered. Ethyl acetate and epichlorohydrin excess were removed on rotary evaporator.

Purification was achieved by silica gel flash chromatography using a gradient of cyclohexane/ethyl acetate mixtures as eluent. The proportion of ethyl acetate was automatically and gradually increased from 0% to 100% to separate all fractions.

2.3. Oligomerization reaction

The optimal experimental conditions for the preparation of oligomers **4** from **2** and **3** were determined by DSC. Mixtures of **2** and **3** (1/1) and catalyst (from 0 to 10 w.% of the total mass) were placed in sample pans to investigate the effects of the catalyst amount. The time needed to reach the completion of the reaction was also determined. Once the experimental conditions were set, glass vessels were filled with **2** (1.0 eq.), **3** (from 1.1 to 2.0 eq.) and triphenylbutylphosphonium bromide (5 w.% of the total weight). The mixtures were placed in an oil bath and magnetically stirred for 2 h at 125 °C.

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