



Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin



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ABSTRACT

Novel biobased epoxy thermoset was synthesized from gallic acid, a phenolic acid encountered in various plants, both in its simple form and as a part of gallotannins. The functionalization of gallic acid was carried out using a two-step synthesis involving the allylation of OH groups followed by the epoxidation of resulting double bonds. The performance of two oxygen transfer agents (*meta*-chloroperbenzoic acid (*m*CPBA) and methyl(trifluoromethyl) dioxirane generated in situ from 1,1,1-trifluoroacetone and oxone) was evaluated in the epoxidation of the allylic double bonds. The glycidyl derivative of gallic acid (GEGA) obtained from *m*CPBA epoxidation was cured in epoxy polymer formulation with isophorone diamine (IPDA). The thermal and mechanical preliminary analyses showed that this new epoxy network based on GEGA displayed interesting properties compared to the epoxy polymer formulated with commercial diglycidyl ether of bisphenol A (DGEBA). A higher glass-transition temperature of GEGA/IPDA epoxy resin indicates a higher crosslinking density of this network.

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1. Introduction

Epoxy resins constitute a major class of thermosetting resins and are extensively used as coatings, electronic materials, adhesives. Owing to their outstanding mechanical and electrical properties, chemical resistance, adhesion, and minimal shrinkage after curing [1], they are used in structural applications as well. Most of these thermosets are industrially manufactured from bisphenol A (BPA), a compound that was initially synthesized as a chemical

oestrogen [2]. The aromatic ring of BPA is particularly suitable since it confers a good thermal resistance to epoxy resins. But this endocrine disruptor can mimic the body's own hormones and may lead to several negative health effects [3–6] including alterations in both immune and reproductive systems along with a modification in brain chemistry [7]. The negative impact of BPA on human health and environment necessarily implies to focus the researches for the substitution of BPA especially since some countries, such as Canada or France, have recently banned the use of BPA in food contact materials. Therefore, there is an increasing interest of chemical industry for non-harmful aromatic compounds allowing the synthesis of epoxy thermosets without BPA.

Moreover, with the limitation and high costs of fossil resources, renewable resources keep being in common

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interest of both academic and industrial laboratories at the time. Hence, biomass is a potential source of biopolyphenols which could lead to the production of heat resistant cross-linked epoxy thermosets and overcome petroleum-based BPA. Natural polyphenols which are very abundant in forest/agricultural biomass or residues [8] are structurally similar to materials already employed for this purpose.

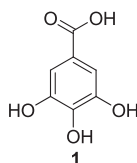
Some studies have reported the use of natural polyphenols in thermosetting applications. Lignins co-produced during papermaking were formulated with epoxy networks and cross-linked by direct heating [9–12]. Research works at IBM reported the incorporation of lignin into epoxy polymers used in the fabrication of printed wiring boards for the microelectronics industry [13]. However, none of these works aim at functionalizing directly lignin to epoxy reactants, probably because of the poor solubility of this polymer in organic solvents.

The other terrestrial source of phenolic compounds is tannins. These biopolyphenols exhibit a wide structural diversity and have generally more than two phenolic hydroxyl groups, but this is not a drawback in the perspective of cross-linked epoxy thermosets, which constitute the main applications.

In our previous research, one of the building blocks of polymeric condensed tannins, namely catechin, was reacted with epichlorohydrin in alkaline medium to give the expected tetraglycidylether of catechin along with a benzodioxane derivative. The formation of this cyclic by-product is directly related to the catechol ring (B ring) within the catechin structure. Indeed, the oxirane ring introduced in the first substitution step undergoes an intramolecular nucleophilic attack from the second phenolate anion located in *ortho* position to yield the benzodioxane-type derivative. In fact, catechin derivatives with three methyloxirane functions on average were actually obtained [14].

In 1985 Haruo Tomita et al., disclosed in their invention the use of gallic acid (a phenolic acid occurring free or as a part of gallotannins in different plants) as a phenolic source in the epoxy thermosets production [15].

In this patent, gallic acid **1** (Scheme 1) was reacted with epichlorohydrin in the presence of a phase transfer catalyst and in the substantial absence of water, thereby causing addition reaction of epichlorohydrin to carboxyl group and at least one phenolic hydroxyl group to occur. Surprisingly, the vicinity of the phenolic hydroxyl groups in the gallic acid structure does not allow the formation of by-products (or they have not been described in the patent). Thus, the chemical reactivity is dependent in a very subtle way on the chemical structure of a given component.



Scheme 1. The gallic acid chemical structure.

Gallic acid **1** contains three phenolic hydroxyl groups and one carboxylic group which can be exploited in order to obtain new biobased epoxy thermoset with improved thermal and mechanical properties.

Therefore, to overcome the incomplete functionalization of the phenolic hydroxyl groups of gallic acid by epichlorohydrin, we investigated another route to gallic acid glycidylation based on a two-step chemical synthesis: the alkaline assisted allylation of hydroxyl groups followed by the epoxidation of the resulting double bonds. Two oxygen transfer agents were compared in the epoxydation of the allylic double bonds: *meta*-chloroperbenzoic acid (*m*CPBA) and methyl(trifluoromethyl) dioxirane generated in situ from 1,1,1-trifluoroacetone and oxone. The efficiency of each reagent to produce the full glycidated derivative of gallic acid was evaluated.

The glycidylated product was then cured with commercial 3-aminomethyl-3,5,5-trimethyl cyclohexylamine (Isophorone diamine: IPDA) to estimate its capacity to yield a cross-linked material. The thermal properties of the resulting epoxy network were compared to the standard diglycidyl ether of bisphenol A (DGEBA) epoxy polymer.

2. Experimental

2.1. General

Gallic acid (97.5%), allyl bromide (99.0%), isophorone diamine (IPDA, $\geq 99.0\%$), *meta*-chloroperbenzoic acid (*m*CPBA, $\leq 77.0\%$), Trifluoroacetone (97.0%), Oxone™ monosulfate compound, sodium bicarbonate ($\geq 99.5\%$), CH₃CN (99.8%), DMF (99.8%) and CH₂Cl₂ (99.8%) were purchased from Sigma–Aldrich. The conventional petroleum-based epoxy monomer used was a diglycidyl ether of bisphenol A (DGEBA) supplied by Aditya Birla Chemicals (Epotec), with an Epoxide Equivalent Weight (EEW) of 182 g/equiv. The IPDA Amine Equivalent Weight (AEW) is 42 g/equiv.

All the reactions were monitored by thin layer chromatography (TLC). TLC was performed on silica gel 60 F254. ¹H and ¹³C NMR spectra were recorded in DMSO-*d*₆, CDCl₃ and Acetone-*d*₆ solutions at 500 MHz using a VARIAN Unity-Inova spectrometer. Chemical shifts are reported in ppm relative to DMSO-*d*₆ [signals for residual DMSO-*H*₆ in the DMSO-*d*₆: 2.50 for ¹H NMR and 39.4 for ¹³C NMR], CDCl₃ [signals for residual CHCl₃ in the CDCl₃: 7.26 for ¹H NMR and 77.0 for ¹³C NMR] and Acetone-*d*₆ [signals for residual Acetone-*H*₆ in the Acetone-*d*₆: 2.05 for ¹H NMR and 30.83 for ¹³C NMR]. ESI-MS analyses in positive mode were performed using a Bruker Daltonics Ion trap mass spectrophotometer (Bremen, Germany).

2.2. Allylation of gallic acid

A 100 mL two-necked flask equipped with a septum cap and a magnetic stirring bar was charged with 30 mL of DMF and 0.68 g (4 mmol) of gallic acid. The solution was cooled with an ice bath and potassium carbonate (2.21 g, 16 mmol) was added. After three minutes, allyl bromide (1.4 mL, 16 mmol) was added dropwise by a syringe. The solution was stirred for 30 min at 0 °C and then at room

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