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Design and synthesis of biobased epoxy thermosets from biorenewable resources

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ABSTRACT

Biobased diepoxy synthons derived from isoeugenol, eugenol or resorcinol (DGE-isoEu, DGE-Eu and DGER, respectively) have been used as epoxy monomers in replacement of the diglycidyl ether of bisphenol A (DGEBA). Their curing with six different biobased anhydride hardeners leads to fully biobased epoxy thermosets. These materials exhibit interesting thermal and mechanical properties comparable to those obtained with conventional petrosourced DGEBA-based epoxy resins cured in similar conditions. In particular, a high T_g in the range of 90–130 °C and instantaneous moduli higher than 4.3 GPa have been recorded. These good performances are very encouraging, making these new fully biobased epoxy thermosets compatible with the usual structural application of epoxy materials.

1. Introduction

Thermoset epoxy resins are used in a wide variety of applications, for example, composites, aeronautic and automotive components [1]. Indeed, they have high performances among the available commercial resins. They exhibit excellent adhesion and mechanical properties as well as chemical, electrical and heat resistance. Currently, most of the epoxy resins and hardeners used are derived from oil resources leading to the harmful environmental impact. Moreover, bisphenol A is widely used as a basic building block for the preparation of these epoxy resins, in particular, the well-known diglycidyl ether of bisphenol A (DGEBA). However, bisphenol A was recently proved to be an endocrine-disrupting chemical [2,3] and a water contaminant [4]. Therefore, its substitution with biobased building blocks is strongly encouraged, which would also reduce the petrochemical contribution [5].

During the last decades, many studies were devoted to develop a wide variety of molecules for the preparation of sustainable epoxy resins [6,7]. A part of this work concerns the replacement of DGEBA in epoxy resins. The authors were obviously interested in synthesizing diepoxy components containing rigid aromatic rings to obtain polymers with high modulus and high glass transition temperatures. For this purpose, Auvergne et al. [8] and also Ding and Matharu [9] reviewed the potential of polyphenols and

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tannins. More recently, Aouf et al. [10,11], Yang et al. [12] and Shibata and Ohkita [13] reported biobased diepoxy resins obtained, respectively, from functionalization of gallic and vanillic acids, plant-based phenolic acids or vanillin derivatives. An alternative way to produce eugenol-based epoxy resins was proposed by Qin et al. [14] and Wan et al. [15,16]. Other appropriate candidates are molecules extracted from lignin, which are very competitive to DGEBA-based thermosets as reviewed by Llevot et al. [17] and Ferdosian et al. [18]. Recently, such a lignin-based epoxy resin was reported for potential application in epoxy asphalt [19]. Thus, lignin-based epoxy resins are currently the subject of innovative and intense investigations [20].

In this context, we recently described a suitable lignin synthon for epoxy thermoset applications, 2-[3-methoxy-4-(2-oxiranylmethoxy)phenyl]-3-methyloxirane, named DGE-isoEu [21]. This new biobased monomer was prepared according to a two-step procedure, from isoeugenol, catalytically fragmented from lignin. Diepoxy derivative of isoeugenol (DGE-isoEu) was cured satisfactorily with acid derivative hardeners to obtain thermosetting epoxy polymer having high T_g and promising mechanical properties. Continuing our approach and with the aim to develop fully biobased epoxy thermoset materials, the curing of the DGE-isoEu with biobased anhydride hardeners is studied in this article. Compared with the classical diamine hardeners, these curing agents present several major advantages. First, they avoid the use of toxic aliphatic diamine. Moreover, as reported by Paramarta and Webster [22], anhydride hardeners are preferred to diamines for their higher reactivity, especially in the case of internal DGE-isoEu epoxide that is less reactive as compared to terminal epoxide. Furthermore, to reduce the environmental impacts of the epoxy thermosets, the curing agents used in this study are synthesized with high yield from biorenewable and inexpensive dicarboxylic acid agents [23]. Recently an innovative route to renewable anhydrides from biobased furanics has also been described by Thiyagarajan et al. [24]. It is worth noting that recently much attention has also been paid to biobased amine hardeners as reviewed by Froidevaux et al. [25] and Fache et al. [26]. It is also noticeable that, after curing, some of the tested hardeners still contain a rigid cycle: this is anticipated to produce epoxy thermosets with high glass temperature and high modulus.

In this article, DGE-isoEu or diepoxy derivative of eugenol (DGE-Eu) was successively cured with six biobased anhydride hardeners: the resulting materials were analysed using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and nanoindentation. These results were compared with those obtained by curing commercially available epoxy resins (DGEBA and the biobased diglycidyl ether resorcinol [DGER] resin) with six anhydride hardeners.

2. Experimental section

2.1. Materials

DGE-isoEu was prepared from biobased isoeugenol [27] and biobased epichlorohydrin [28] according to our previously published procedure [21]. DGE-Eu was obtained as recently reported by Qin et al. [14]. XRD single-crystal analysis of DGE-Eu was recently resolved by some of us [29]. DGEBA and DGER were purchased from Sigma–Aldrich.

Six anhydride curing agents were synthesized according to Ref. [23]: diphenic anhydride (DPA), glutaric anhydride (GA), phthalic anhydride (PA), camphoric anhydride (CA), succinic anhydride (SA) and itaconic anhydride (IA). Anhydrides were used after the purification step (separation from $MgCl_2$ by sublimation). 1,2-Dimethylimidazole (DMID, 95% purity) was purchased from Sigma–Aldrich and was used without any further purification.

Molecular representations of reagents used in the resin manufacturing process are presented in Figs. 1 and 2.

2.2. General methods and instrumentation

2.2.1. Fourier transform infrared spectroscopy

FT-IR spectra were recorded using a Brucker Vector 22 fitted with a specac MKII Golden Gate Diamond Attenuated Total Reflectance device equipped with ZnSe lenses in the 4000–500 cm^{-1} wavenumber range (12 scans at spectral resolution of 4 cm^{-1}).

2.2.2. Differential scanning calorimetry

DSC analyses were carried out using TA MDSC 2920 under nitrogen flow (60 mL min^{-1}) with a sample mass of 10 ± 3 mg. To study curing reaction, samples were heated from −20 to 180 °C at a heating rate of 5 °C min^{-1}. To determine glass transition temperature (T_g), the cured resin was heated from −20 to 180 °C at a heating rate of 20 °C min^{-1}.

2.2.3. Thermogravimetric analyses

Thermogravimetric analyses were performed using a TA Instruments TGA Q600 thermoanalyser using aluminium pans. Samples (5–10 mg) were heated from room temperature to 800 °C at a rate of 20 °C min^{-1} under air flow (100 mL min^{-1}). Weight loss percentages were determined using the TA Universal Analysis 2000 software accompanying the instrument.

2.2.4. Nanoindentation mechanical property analyses

Nanoindentation experiments were performed using an ultra nanoindenter from Anton Paar. A Berkovich indenter was used. The area function was calibrated by indenting in a fused silica sample with a known Young's modulus and Poisson's ratio. Before carrying out the tests, the samples were polished with SiC paper, alumina particles until 0.03 mm and then colloidal silica. The instantaneous indentation modulus E_I and hardness H at different indentation depths, the relaxed indentation modulus E_R and finally the strain rate sensitivity m were determined from multicycle indentations, indentation at different constant strain rate $\dot{h}/h$ (where h is the indentation depth) and trapezoidal holding force tests with linear loading and unloading segments. The indentation protocols were the same as used previously [21].

2.2.5. Epoxy resin curing protocol

A comparable protocol as described in our previous work [21] was carried out for each sample of this study. Epoxy

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