



Synthesis and characterization of biobased epoxy monomers derived from D-glucose



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ABSTRACT

This paper reports the preparation of newly synthesized sugar-based epoxy monomers, suitable for replacing petrochemical-derived epoxy resins of high thermal stability. Several bi- tri- and tetrafunctional epoxy components were prepared from D-glucose, among them the glucopyranoside- and glucofuranoside-based trifunctional ones proved to be the most promising for high-tech applications. The applicability of the synthesized compounds as epoxy monomers was investigated by curing probes with a model aromatic amine-type hardener. The curing enthalpy of the bioepoxy resins were examined, and compared to theoretical values, as well as the glass transition temperature, which is a crucial parameter when determining the potential fields of application of the bioresins. T_g values up to 175 °C were reached, while the thermal degradation of the cured resins start at around 300 °C.

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1. Introduction

In recent decades polymers derived from renewable resources became increasingly important as sustainable, eco-efficient and biodegradable products. The aim is to replace, at least partially, certain petroleum-based monomers [1–7], such as diglycidyl ether of bisphenol A (DGEBA), which is used extensively as epoxy component of thermosetting polymers. Recent works on the synthesis and categorization of biobased epoxide materials are thoroughly discussed in the review written by Auvergne et al. [8]. Besides the fossil origin, the recognized estrogenic properties of bisphenol A (BPA) also intensify the research activities in this field [9]. The chemical bonds that link

bisphenol A into the polymer backbone are not completely stable; thus, the polymer may release, with time, a small amount of BPA, which is toxic to living organisms [9].

Synthesis methods for biobased polymers have been developed starting from different natural materials, such as vegetable oil [10–13], fatty acids [14], rosin [15,16], wood biomass [17], industrial lignin [17,18] and starch [19]. From a life-cycle perspective, sugar is a renewable resource that has the potential to be used as an alternative to petroleum-based polymers. At the same time, the development of new high value products and new concepts in sugar manufacturing could be an answer [20] to the challenge of both oversupply and low prices in that field [21].

The presence of highly reactive hydroxyl group in the very common and readily available carbohydrates enables the synthesis of a wide variety of monomers suitable for making different classes of polymers [22–26]. The multifunctionality of these compounds necessitates specific

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group protection if linear polymers with high molecular weight are desired. Carbohydrate-based polycondensates can typically show increased hydrophilicity, lower toxicity and higher susceptibility to biodegradation, compared to those coming from petrochemical feedstock.

Update on the synthesis and application of carbohydrate-containing polymers till 2001 is given in the review written by Linhardt et al. [27], summarizing the knowledge accumulated on the synthetic carbohydrate-based polymers, which are increasingly explored as biodegradable, biocompatible, and biorenewable materials applicable as water absorbents, chromatographic supports, and medical devices. Later on, L-arabinitol- and xylitol-based polymers [28,29], and D-mannitol-, galactitol- and galactaric acid-based polyesters [30–32] have been prepared. Synthesis and characterization of polyurethane from a D-glucamine-based monomer [33], as well as that of polyamides from galactaric, xylaric, D-glucaric and D-mannaric acids [34–36] have been also reported.

Regarding epoxies, the use of natural polysaccharides was investigated in the synthesis of biobased epoxy monomers aiming to replace DGEBA. One group of the most promising sugar-derivatives as starting material are dianhydrohexitols, such as isosorbide, isomannide, isoidide, derived from D-glucose, D-mannose and L-fructose, respectively. The synthesized diglycidyl ether of isosorbide (1,4:3,6-dianhydro-D-sorbitol) was successfully incorporated into thermosets and thermoplastics in several cases. Some isosorbide-based thermosets had dry mechanical properties comparable to DGEBA [37–41], however, the glass transition temperatures of the amine-cured networks are still lower than expected [40–42].

The aim of the present work was to establish innovative biobased structures with good performances by preparing epoxy components derived from D-glucose, an inexpensive, easily available and renewable starting material, which has not yet been applied as epoxy monomer precursor. The characterization of their curing properties, glass transition temperature and thermal stability was also targeted.

2. Experimental

The materials used in the organic syntheses, as well as the applied model curing agent, DDM (4,4'-diaminodiphenyl methane, amine hydrogen equivalent weight: 49.6 g/eq) were purchased from Sigma–Aldrich. As reference epoxy component DGEBA was applied (ER 1010, epoxy equivalent weight: 180 g/eq; viscosity: 12 Pa s), received from IpoX Chemicals.

The viscosity of the synthesized liquid epoxy monomer was determined in steady state flow rotating mode at room temperature, using a TA Instruments AR2000 rheometer. The shear rate was between 4 and 40 s⁻¹, the sample was placed between a rotating 40-mm-diameter plane disc and a controlled-temperature plane sheet. 5 points have been recorded in each decade of shear rate, 3 min have been left at each point to reach equilibrium, and 3 consecutive measurements had to be in a 5% difference range before continuing to the next shear rate point. The curing process was monitored with TA instruments DSC Q2000

type DSC equipment in 50 ml/min nitrogen flow. Tzero type aluminum pans were used, the sample size was between 5 and 10 mg. The applied three-step temperature program consisted of heat/cool/heat cycles: after a linear ramp from 25 to 250 °C with 5 °C/min heat rate, the sample was cooled down to 0 °C with 50 °C/min cooling rate, followed by a second linear heating ramp from 0 to 250 °C with 5 °C/min heating rate. From the first ramp the curing enthalpy was determined, while from the second one the glass transition temperature of the different systems was received.

The completion of the curing was also monitored by Raman spectrometry, using a Horiba Jobin–Yvon LabRAM system coupled with an external 785 nm diode laser source and an Olympus BX-40 optical microscope. The spectrograph was set to provide a spectral range of 200–2000 cm⁻¹ and 3 cm⁻¹ resolution. Objectives of 10× for the starting materials and 50× magnification for the cured sample were used for spectrum acquisition.

The thermal stability of the different compositions was determined by TGA measurements using Setaram Labsys TG DTA/DSC instrument in the temperature range of 25–800 °C at a heating rate of 10 °C/min under nitrogen gas flow rate of 30 ml/min. About 15–20 mg of sample was used in each test.

Shore D hardness of several cured epoxy networks was investigated using a Zwick Roell H04.3150 type hardness tester. At least ten points of each sample were tested, according to ISO 868.

Specimens for the Raman and hardness measurements of the synthesized trifunctional bioepoxy resins and the reference DGEBA were cured in silicon mold, with a temperature program of 2 h at 120 °C and 2 h at 150 °C.

3. Results and discussion

3.1. Synthesis of D-glucose-based epoxy components

In this part, the syntheses of α -D-glucopyranoside- and glucofuranoside-based epoxy monomers derived from D-glucose are presented. Glucose is an easily available commercial product and it is a “green”, inexpensive and non-toxic starting material in organic syntheses.

Our aim was to prepare D-glucose-derivatives with two or more epoxy groups making them suitable for polymerization. The exact recipes of the synthetic procedures can be found in [Supplementary data](#).

Methyl- α -D-glucopyranoside (that is a commercial product) can be obtained by the condensation of D-glucose with methanol in the presence of cation-exchange resin as catalyst (yield of the α -D-anomer about 25%) [43]. (Our experiments described here were carried out starting from methyl- α -D-glucopyranoside, but, a mixture of α - and β -anomers is also perfectly suitable for the purpose of the polymers). Methyl 4,6-O-benzylidene- α -D-glucopyranoside (**1**) was prepared in the condensation of methyl- α -D-glucoside with benzaldehyde using zinc chloride as the catalyst ([Scheme 1](#)). After a reaction of 4 h at room temperature, the intermediate **1** was obtained in a yield of nearly 72% by crystallization [44]. Treatment of compound **1** with

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