



High performance bio-based benzoxazine networks from resorcinol and hydroquinone

Ludovic Dumas ^{a,b,*}, Leïla Bonnaud ^a, Marjorie Olivier ^b, Marc Poorteman ^b, Philippe Dubois ^{a,*}

^a Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), Materia Nova Research Center & University of Mons, 23 Place du Parc, B-7000 Mons, Belgium

^b Department of Materials Science, Materials Engineering Research Center (CRIM), University of Mons, 23 Place du Parc, B-7000 Mons, Belgium

ARTICLE INFO

Article history:

Received 15 December 2015

Received in revised form 8 January 2016

Accepted 9 January 2016

Available online 11 January 2016

Keywords:

Benzoxazine

Bio-based

Furfurylamine

Resorcinol

Hydroquinone

ABSTRACT

This work presents a scalable and solventless synthesis of two fully bio-based bis-benzoxazine resins derived from resorcinol, hydroquinone and furfurylamine. The structures of the two synthesized precursors have been studied by ¹H NMR and FTIR spectroscopies and SEC. The polymerization and degradation of the precursors have been investigated and monitored by DSC and TGA. The properties of the resulting polybenzoxazine networks were found to be dependent on the precursor molecular structure. In both cases, an excellent thermomechanical behavior associated with high charring ability were obtained which highlights the great potential of these fully bio-based resins as new matrices for the preparation of structural composites following a sustainable approach.

© 2016 Published by Elsevier Ltd.

1. Introduction

Benzoxazine resins are a class of phenolic resin that benefit a growing interest in the field of thermosetting materials. The characteristic functional group of these resins consists on a heterocyclic six-membered oxazine ring fused to a benzene ring. As firstly prepared by Holly and Cope in 1944 [1] they only enter the field of thermosetting materials in the 90s with the help of Ning and Ishida who popularized their synthesis by a solventless process [2,3]. These new resins offer an excellent balance of material property, combining both the specific advantages of traditional epoxy and phenolic resins. Their henceforth well-known main features are: (i) an easy thermal curing by ring-opening polymerization without the need of hardeners or catalysts, (ii) a limited shrinkage during curing, (iii) a high glass transition temperature, (iv) a low water absorption, (v) a high charring yield, (vi) a low coefficient of thermal expansion and (vii) low dielectric properties [4–7]. The combination of these interesting properties makes benzoxazines an essential resin for the preparation of high-performances materials. Nevertheless, the most relevant characteristic feature of benzoxazine probably relies on the great versatility of monomers molecular design and related chemical functionality. Indeed, as they are readily synthesized by a Mannich-like condensation of an amine, a phenol, and formaldehyde, both the diversity and large choice of possible combinations of reagents allow the preparation of a very wide range of monomers, which can be used in order to tailor or reach specific properties [8]. The number of newly synthesized monomers is thus constantly increasing; however a particular interest for both the academic and industrial researches is driven on those based on renewable or sustainable organic materials as the development of

* Corresponding authors at: Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), Materia Nova Research Center & University of Mons, 23 Place du Parc, B-7000 Mons, Belgium (L. Dumas).

E-mail addresses: ludovic.dumas@outlook.fr (L. Dumas), philippe.dubois@umons.ac.be (P. Dubois).

environmentally compatible and sustainable polymers is one of the current challenges in polymer science [9]. Some bio-based benzoxazines have been already synthesized from bio-based chemicals such as diphenolic acid [10], cardanol [11,12], furfurylamine [13–15], and more recently vanillin [16] and eugenol [17–19]. Interestingly, a short review on bio-based benzoxazine has been published very recently [20]. However, benzoxazines were in most cases only partially bio-based as the counterpart of the molecule, i.e. the amine or the phenol was still petroleum-based derivatives. To the best of our knowledge, only few groups have successfully synthesized fully bio-based benzoxazines. The renewable benzoxazine monomers reported in the literature were synthesized from the combination of furfurylamine or stearylamine with guaiacol [14,21] or furfurylamine with vanillin [22]. Such chemicals can indeed be entirely derived from bio-based feedstocks, while paraformaldehyde can be obtained from bio-methanol as mentioned by these authors. Nonetheless, these monomers consist only on monobenzoxazines and their polymerization cannot lead to a highly crosslinked network. Consequently the thermo-mechanical properties of these fully bio-based thermosets are almost limited by their glass transition temperature.

In order to synthesize fully bio-based benzoxazines with suitable properties for the preparation of high performance materials, two diphenolic compounds were selected and combined with furfurylamine: resorcinol and hydroquinone, respectively benzene-1,3-diol and benzene-1,4-diol. They have been to the best of our knowledge never used for the synthesis of bisbenzoxazine resins. Kiskan and Yagci [23] used resorcinol in order to prepare a monobenzoxazine with a photopolymerizable coumarin group while Oie et al. studied the use of methylresorcinol as a crosslinker for conventional mono benzoxazine. Surprisingly, resorcinol and hydroquinone were not used as potential bio-based bisphenol, probably because they were usually known to be produced from petroleum-derived and carcinogenic benzene. However, in the 2000s alternative biosynthesis processes of these bisphenol have emerged. These interesting new approaches were studied by Frost et al. and consist on the microbial synthesis of phloroglucinol or quinic acid using glucose as raw materials, which are further catalytically converted into resorcinol or hydroquinone [24–26]. Together with catechol, these dihydroxy aromatic precursors can be thus synthesized from nontoxic plant-derived glucose following a sustainable way.

In this contribution, we report for the first time the synthesis of two novel fully bio-based bis-benzoxazine precursors using a straight and upscalable solventless method and show their potential for the preparation of high performance materials.

2. Experimental

2.1. Materials

Furfurylamine (99%), resorcinol (99%), hydroquinone (99%) and paraformaldéhyde (95%) were purchased from Aldrich and used without any further purification.

2.2. Characterizations

The ^1H NMR spectra were recorded with an NMR spectrometer (Bruker, 500 MHz), using deuterated dimethylsulfoxide ($\text{DMSO-}d_6$) as solvent and the chemical shift was calibrated by setting the chemical shift of DMSO as 2.50 ppm.

Calorimetric studies were carried out at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ using a differential scanning calorimeter (DSC Q200 from TA Instruments) under nitrogen flow of $50\text{ mL}/\text{min}$. An Indium standard was used for calibration.

Thermomechanical properties were investigated using a dynamic mechanical thermal analysis (DMTA) apparatus (DMA 2980 Dynamical Mechanical Analyzer from TA Instruments). Specimens ($70 \times 12 \times 3\text{ mm}^3$) were tested in a dual cantilever configuration with a dual cantilever length of 35 mm. The thermal transitions were studied in the temperature range of $25\text{--}370\text{ }^\circ\text{C}$ at a heating rate of $3\text{ }^\circ\text{C}/\text{min}$ and at a fixed frequency of 1 Hz. An amplitude of $18\text{ }\mu\text{m}$ was used corresponding to a strain of 0.043%. One representative sample was used for the measurements.

Thermogravimetric analysis (TGA) was used to study the anaerobic thermal degradation of the cured systems. Approximately 10 mg of the sample was submitted to a temperature ramp from 25 to $1000\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under a nitrogen flow of $60\text{ mL}/\text{min}$. All TGA experiments were performed by using a TGA Q50 device from TA Instruments.

Gel Permeation Chromatography (GPC) was performed in CHCl_3 at $35\text{ }^\circ\text{C}$ using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 with a flow rate of $1\text{ mL}/\text{min}$, a differential refractive index detector ERMA 7517, and two PL gel Mixed-B $10\text{ }\mu\text{m}$ columns. PS standards were used for calibration.

Fourier transform infrared (FTIR) spectra were recorded in transmission mode using a Bruker IFS 66v/S spectrometer equipped with a vacuum apparatus. Precursors and crosslinked polymers were powdered and dispersed into a KBr matrix with a weight concentration of about 1 wt%. Spectra were recorded under vacuum from $500\text{ to }4000\text{ cm}^{-1}$ with a wavenumber resolution of 4 cm^{-1} . 64 scans were collected for each sample.

2.3. Preparation and characterization of resorcinol-based benzoxazine precursor, R-Fa

This procedure stems from the ones described by Ishida et al. [3] but the addition order of reagents was changed in order to prevent the condensation reaction between bisphenols and formaldehyde and the subsequent formation of phenol-formaldehyde resin. Resorcinol 20 g ($1.798 \cdot 10^{-1}\text{ mol}$) and furfurylamine 35.3 g ($3.596 \cdot 10^{-1}\text{ mol}$) were mixed with a

Download English Version:

<https://daneshyari.com/en/article/7804836>

Download Persian Version:

<https://daneshyari.com/article/7804836>

[Daneshyari.com](https://daneshyari.com)