European Polymer Journal 81 (2016) 337–346

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Chavicol benzoxazine: Ultrahigh Tg biobased thermoset with tunable extended network

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ARTICLE INFO

Article history:
Received 2 May 2016
Received in revised form 21 June 2016
Accepted 23 June 2016
Available online 25 June 2016

Keywords:
Benzoxazine
Bio-based
Chavicol
Allyl-benzoxazine
Tunable network

ABSTRACT

A novel biobased benzoxazine monomer containing additional allyl functionality was synthesized using a solventless approach from the reaction of a natural occuring phenol: chavicol, *para*-phenylene diamine and formaldehyde. The chemical structure of this functionalized benzoxazine monomer was confirmed by ^{1}H NMR and FTIR. Its polymerization was investigated and monitored by DSC showing two well defined exotherms allowing the selective ring-opening polymerization of benzoxazine functions and the preservation of the allyl functionality. The network crosslink density could be further increased via the controlled polymerization of allyl functionalities with a post-cure in order to adjust the thermo-mechanical properties. When both networks were polymerized, the thermoset presented an excellent thermo-mechanical stability with a Tα higher than 350 °C as measured by DMTA. This exceptional behavior for a potentially biobased benzoxazine resin will allow the preparation of sustainable high performance biocomposite materials.

1. Introduction

Benzoxazine resins represent a relatively novel class of thermosets that currently benefit renewed growing interest as they allow for combining the advantages of both traditional epoxy and phenolic resins. The characteristic functional group of these resins consists in a heterocyclic six-membered oxazine ring fused to a benzene ring. First prepared by Holly and Cope [1], Ning and Ishida demonstrated their real interest for materials purposes in the 90s by introducing a solventless synthesis process and highlighting their excellent balance of material properties [2,3]. 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 constants [4–7]. Nevertheless, the main interesting characteristic of benzoxazines is their easy and versatile synthesis by a Mannich-like condensation of three compounds: a phenol, an amine and formaldehyde offering thereby an extraordinary monomer design flexibility that allows for tailoring a large range of properties [8]. The number of newly synthesized monomers is therefore constantly increasing, in particular by including extra functionalities in order to provide additional specific properties. Furthermore the development of biobased and renewable organic materials is one of the hot current challenges in polymer science and is of particular interest

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http://dx.doi.org/10.1016/j.eurpolymj.2016.06.018
0014-3057/

for both academics and industrials [9]. Benzoxazine resins are by no means an exception and have recently become new players in the biobased polymers arena where researchers make an effort for replacing commercially available and inexpensive phenols and amines by natural products without significant loose of material properties. Various bio-based benzoxazines have already been synthesized from bio-based phenol such as diphenolic acid [10], cardanol [11–13], guaiacol [14,15], vanillin [16,17], eugenol [18–20], coumaric, ferulic and phloretic acids [21] or also resorcinol [22] while the most used amines were furfurylamine [14,23,24], and stearylamine [13,14]. Interestingly, a short review on biobased benzoxazine has been published very recently [25]. From these natural compounds, eugenol (4-allyl-2-methoxyphenol) appeared to present a high potential for green chemistry due to its realistic availability and low production cost [19], but benzoxazines synthesized with this trisubstituted aromatic ring were unable to homopolymerize correctly due to the occupied *ortho* and *para* positions [19,26]. Moreover, the thermal stability of eugenol-based benzoxazines was too low to allow the homopolymerization of the allyl function without addition of a comonomer or introduction of extra polymerizable sites [19,20].

In order to keep the interest to use an allyl phenol, eugenol can be replaced by another naturally occurring phenol, namely 4-allyl-phenol (chavicol), which to the best of our knowledge has never been studied to prepare benzoxazine resins. Interestingly, chavicol can be found in betel oil, bay oil or in sweet basil [27,28]. Other articles or patents describe also the possible enzymatic conversion of *para*-coumaryl/coniferyl alcohol esters, present in lignin, into chavicol but the processes are not yet easily scalable nor industrials [29,30].

Herewith we propose the synthesis of a potentially bio-based chavicol benzoxazine presenting the ability to be polymerized selectively through the ring opening reaction of benzoxazine rings and to further extend the network crosslinkability with the thermally activated reaction of the allyl functions. This selective crosslinking reaction allows an easy tuning of the network properties.

2. Experimental

2.1. Materials

The following chemicals were purchased from Aldrich and used without any further purification: 1,4-phenylenediamine (99%), paraformaldehyde (95%). 4-allylphenol (95%) was purchased from Chembo Pharma and used as received. Ethanol was purchased from VWR.

2.2. Characterization

The ^{1}H NMR spectra were recorded with a NMR spectrometer (Bruker, 500 MHz), using deuterated dimethylsulfoxide (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 °C/min using a differential scanning calorimeter (DSC Q200 from TA Instruments) under nitrogen flow of 50 mL/min. An indium standard was used for calibration.

Thermogravimetric analysis (TGA) was used to study the anaerobic thermal degradation of the precursor blends and cured systems. Approximately 10 mg of the sample was submitted to a temperature ramp from 25 to 1000 °C at a heating rate of 10 °C/min under a nitrogen flow of 60 mL/min. All TGA experiments were performed by using a TGA Q50 device from TA instruments.

Thermo-mechanical properties were investigated using a dynamic mechanical thermal analysis (DMTA) apparatus (DMA 2980 Dynamical Mechanical Analyzer from TA Instruments). Specimens ($70 \times 12 \times 3$ 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 25–370 °C at a heating rate of 3 °C/min and at a fixed frequency of 1 Hz. An amplitude of 18 μm was used corresponding to a strain of 0.043%. One representative sample was used for the measurements.

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 diluted into a KBr matrix with a weight concentration of about 0.5 wt%. Spectra were recorded under vacuum from 500 to 4000 cm^{-1} with a wavenumber resolution of 4 cm^{-1}. 64 scans were collected for each sample.

Preparation and characterization of the chavicol-based benzoxazine, C-pPDA.

The C-pPDA synthesis has been adapted from a procedure reported by Ishida [3] chavicol 24.42 g (1.73×10^{-1} mol) and 12.02 g (3.80×10^{-1} mol) paraformaldehyde, 10% in excess, were introduced in a beaker at 50 °C. The mixture was stirred with a mechanical stirrer leading to the formation of a homogeneous white solution. 9.35 g (0.86×10^{-1} mol) 1,4-phenylenediamine, finely powdered, was then added into the beaker and immersed in an oil bath preheated at 120 °C. The addition of the diamine leads to the gelation of the mixture resulting from the condensation of the aromatic diamine and formaldehyde and the subsequent formation of a triazine network [31,32]. At this temperature, the triaza compound reacts quickly with chavicol and the gel is destroyed in a couple of minutes. The mixture was allowed to react for 25 min under continuous stirring. The crude reaction product was then dissolved in refluxing ethanol (~600 mL). Then, the resin was allowed to precipitate upon cooling. The precipitate was collected whereas the filtrate was partially evaporated to allow a second precipitation of the residual soluble C-pPDA. Both precipitates were collected and rinsed with cold ethanol