European Polymer Journal 73 (2015) 344–362

Contents lists available at ScienceDirect

European Polymer Journal

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

Amine hardeners and epoxy cross-linker from aromatic renewable resources

Maxence Fache, Camille Montérémal, Bernard Boutevin, Sylvain Caillol *

Institut Charles Gerhardt, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France

ARTICLE INFO

Article history:
Received 25 September 2015
Received in revised form 28 October 2015
Accepted 29 October 2015
Available online 30 October 2015

Keywords:
Amine hardener
Vanillin
Furfural
Bio-based
Epoxy

ABSTRACT

Bio-based epoxy thermosets are currently extensively investigated. To be industrially relevant, bio-based epoxy formulations must be tailored so that the properties of the resulting thermosets can be conveniently controlled. This can be achieved by choosing the right hardener. Amine hardeners were thus synthesized from potentially bio-sourced vanillin and furfural. These compounds are also aromatic, an important structural feature to reach good thermo-mechanical properties. A tri-functional, vanillin-derived epoxy cross-linker was also synthesized. Multi-functional epoxy monomers can increase the cross-linking density of the network, which is another convenient way of controlling the final properties. Epoxy thermosets were prepared from bio-based epoxy monomers and hardeners, as well as from reference compounds commonly used in industry. These polymers were characterized and structure–property relationships are discussed.

1. Introduction

Epoxy thermosets are an important class of polymers in industry. They are used in many different applications such as coatings in the marine, automobile, or food-packaging industries, or as matrices in structural composites [1]. They are also used as adhesives, or in the electronic industry, for example in printed wiring boards [1]. These applications take advantage of the versatility of epoxy polymers. Indeed, they can be tailored to achieve the specific properties required by these various applications. Epoxy polymers can provide thermosets with excellent mechanical strength and toughness; outstanding chemical, moisture, and corrosion resistance; good thermal, adhesive, or dielectric properties [1].

Many epoxy thermosets are prepared from the reaction of an epoxy monomer or pre-polymer (resin) with a co-monomer (hardener). 75% of the epoxy resins produced worldwide are based on the diglycidylether of bisphenol A (DGEBA) [1]. Bisphenol A is a category 1B (presumed) reprotoxic compound under EU regulation [2]. Thus, its substitution in epoxy thermosets attracted a lot of attention recently [3–7]. In addition, a more general drive for the substitution of petro-based compounds by bio-based ones is also a very actively investigated area of research.

Preparing epoxy thermosets from renewable resources is a burning issue as it would address both problematics at the same time. This issue has thus received significant attention from researchers worldwide [8–11]. The most studied biomass-derived raw materials are vegetable oils [12] and cycloaliphatic compounds like isosorbide [7]. However, in certain thermo-mechanically demanding applications, aromatic raw materials are needed to impart the required properties to the thermoset (high T_g for instance). Therefore, bio-based aromatics are needed to prepare renewable epoxy thermosets. DGEBA

---

* Corresponding author.
E-mail address: sylvain.caillol@enscm.fr (S. Caillol).

http://dx.doi.org/10.1016/j.eurpolymj.2015.10.032
0014-3057/© 2015 Elsevier Ltd. All rights reserved.

itself is a bis-phenolic compound. Bio-based aromatics – more specifically phenolics – are thus also needed in the context of bisphenol A substitution.

The most available sources of phenolics in nature are lignin, tannins, and cashew nutshell liquid (CNSL) [13]. CNSL is composed of phenols substituted with a C_{15} alkyl chain [14]. This long aliphatic segment confers flexibility and thus does not solve the problem of thermo-mechanical properties. Lignin and tannins are poly(phenolics) with a complex and variable structure. Their functionalization and use as epoxy resins, even if investigated [15,16], are made tricky by their variable, polymeric nature, and are thus not mature technologies yet.

Molecular aromatics obtained on a large scale from renewable resources are scarce. Vanillin obtained from lignin depolymerization is one of the only biomass-derived molecular phenol available at an industrial scale (15% of the worldwide production) [2,17]. It is also non-hazardous. Therefore, the use of this compound for renewable polymer synthesis recently attracted a lot of attention [18]. The contributions of our team on this subject dealt mainly with the use of vanillin as a bio-based building-block to prepare epoxy thermosets with good properties [3,19–21]. This approach is continued in this work.

Furfural is an interesting bio-based compound obtained by the acidic dehydration of pentoses, for instance xylose [22]. It is widely available and has been identified as a key renewable building-block, from which other bio-based compounds can be prepared [22,23]. The furanic moiety displays interesting features such as aromaticity and the ability to act as diene in Diels–Alder reactions. Furanic compounds have already been employed to prepare epoxy thermosets with good properties [24–26]. Both vanillin and furfural are bio-based aromatic aldehydes that can be further functionalized to prepare compounds relevant for epoxy thermosets.

Versatility is one of the strong points of epoxy polymers. Reaching different properties can be achieved in many different ways. One of these methods, convenient from an industrial standpoint, is to increase the overall functionality of a given epoxy formulation to increase the cross-link density, and thus reach a higher T_g. Adding a tri- or tetra-epoxy compound to a difunctional epoxy resin increases the overall functionality. Multi-functional epoxy compounds are thus of high industrial importance.

Hardeners can also play a major role to enhance the thermo-mechanical properties of epoxy thermosets. The main epoxy hardeners include mercaptans, carboxylic acids, anhydrides, amines, and phenols [1]. Amines are the most used ones [1], and are used for different purposes depending on their structures. Aliphatic amines are very reactive and can even provide room-temperature curing [27]. The main advantage of cycloaliphatic amines is their versatility: they display a good balance between reactivity and final properties. Aromatic amines are the least reactive but provide good heat and chemical resistance [27]. Hardener structure and functionality strongly impact the material final properties. Having a large range of hardeners with various structures, functionalities, and reactivity to modulate the properties of epoxy thermosets is of the highest importance. Amine hardeners based on various bio-resources, such as amino-acids (tryptophan, lysine) [28,29], vegetable oils [12], isosorbide [30], or chitosan [31] are scarce in the literature. Only few bio-based commercial solutions exist and they are only partially bio-based (e.g. Mannich adducts of cardanol (phenalkamines), or poly(amido-amines) prepared by amidification of fatty acids dimers).

To be accepted as viable solutions, bio-based epoxy formulations need to offer the same versatility as current formulations. To modulate the final properties of epoxy thermosets as much as it is done today with petro-based hardeners, the range of bio-based amine hardeners available to choose from must be increased. In addition, it is also of the highest importance to compare the properties these new hardeners provide with currently existing systems.

The present work thus aims to:

1. Synthesize new, potentially bio-based amine hardeners from furfural and vanillin, use them to prepare bio-based epoxy thermosets, and investigate the structure–property relationships of the polymers.
2. Synthesize a bio-based tri-epoxy compound and investigate its potential as an epoxy cross-linker to increase the T_g of bio-based epoxy thermosets.

2. Experimental

2.1. Materials

Furfurylamine **1** (⩾99%), acetone (⩾99.5%), HCl (⩾37 wt.%), hydroxylamine hydrochloride (99%), anhydrous sodium acetate (99%), activated Pd/C (10 wt.%), sodium percarbonate ($Na_2CO_3{\cdot}1.5H_2O_2$, available H_2O_2 20–30%), TriEthylBenzylAmmonium Chloride (TEBAC, 99%), sodium hydroxide (NaOH, ⩾98%), and all solvents used were purchased from Sigma–Aldrich. Vanillin **4** (99%) was purchased from ABCR. Epichlorohydrin (⩾99%) was purchased from Fluka. All reactives were used as received.

^1H NMR spectra were recorded at a frequency of 400.2 MHz and ^{13}C (APT mode) NMR spectra at a frequency of 100.6 MHz on a Bruker Aspect Spectrometer at room temperature. Deuterated solvents used are given for each molecule. Chemical shifts are in ppm. Silica gel flash chromatography was performed on a Grace Davison Reveleris instrument.