Polymer 116 (2017) 191–203

Contents lists available at ScienceDirect

Polymer

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

Latent curing of epoxy-thiol thermosets

Ali Osman Konuray*, Xavier Fernández-Francos, Xavier Ramis

Thermodynamics Laboratory, ETSEIB, Universitat Politècnica de Catalunya, Av. Diagonal 647, 08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 9 February 2017
Received in revised form
21 March 2017
Accepted 24 March 2017
Available online 30 March 2017

Keywords:
Epoxy-thiol
Click reaction
Curing kinetics
Photobase
Latency

ABSTRACT

Epoxy-thiol curing is a click reaction which allows quantitative yield of the end products. The base-catalyzed reaction is rapid at low temperatures so it is most often desirable to harness reactivity by using latent catalysts. In this work, we used triazabicyclodecene tetraphenylborate ($TBD \cdot HBPh_4$) as a photobase generator (PB). We activated the PB either thermally or by UV light and monitored reaction kinetics by DSC and FTIR methods. Depending on the catalytic system used, the rate of the thiol-epoxy reaction was ordered as follows: Neat base > UV activated PB > thermally activated PB > uncatalyzed system. A series of isothermal and non-isothermal DSC experiments were run on non-irradiated and irradiated samples in order to study the effect of PB content and UV irradiation duration on PB activation efficiency and latency/storage stability. The data from DSC were analyzed using model-free linear isoconversional methods to estimate kinetic parameters such as activation energies. In addition, the kinetics data for both activation methods were shown to be accurately represented by multi-term Kamal models. The storage stability of the systems were studied at room temperature and was shown to fit well to the predictions of the kinetic model.

1. Introduction

Epoxy resins are one of the most used polymeric resins due to their superior performance in many industrial applications. They can be formulated as two-pack systems with a wide selection of curing agents including amines, amides, phenols, carboxylic acids, anhydrides and thiols [1]. Epoxy-thiol systems have been studied relatively less, despite their advantages such as high yield of the curing reaction, superior mechanical properties of end products [2], and their numerous industrial uses such as adhesives, nanocomposites, shape-memory materials and biomedical materials [3,4].

The curing of epoxy resins by thiols proceeds through a click reaction which allows quantitative yield of the epoxy-thiol thermoset. Although the reaction can take place at elevated temperatures without requiring any catalyst, lower curing temperatures can be achieved by using base catalysts. In the base catalyzed epoxy-thiol reaction, the base helps generate thiolate anions by deprotonating thiols. In turn, the thiolate anions couple with the epoxide groups through a nucleophilic ring opening reaction. The resulting alcoholate anions are protonated either by the base catalyst or the thiol to yield the desired reaction products. The reaction exhibits auto-catalytic behavior due to the hydroxyl groups formed [4,5]. Consequently, any further kinetic study of this reaction must account for this effect. The reaction steps for the base-catalyzed reaction are shown in Scheme 1. An alternative reaction scheme involving the nucleophilic attack of the tertiary amine to the epoxy ring as initiation step was proposed by Loureiro et al. [6] which was found to be operative in the curing of thiol-epoxy formulations using a weak base such as 1-methylimidazole [7].

Epoxy-thiol systems catalyzed by bases have fast initial curing rates which lead to undesirably short pot-lives. In order to prepare one-pack formulations, latent catalysts must be used. These catalysts, as the name implies, have latent activity which can only be initiated by external stimuli such as heat or irradiation. They allow storage stability and provide freedom to start the curing reaction whenever desired. In a recent paper, latent thiol-epoxy formulations were developed making use of encapsulated imidazole and urone catalysts that are activated upon heating [3]. Another feasible solution is the use of photobase generators (PB) [8–11]. A PB releases a catalytic base upon UV irradiation which, in turn, initiates the curing reaction. In our work, we use triazabicyclodecene tetraphenylborate ($TBD \cdot HBPh_4$) as a PB [12]. Upon photolysis, $TBD \cdot HBPh_4$ releases triazabicyclodecene (TBD), a strong base, with a pKa of 20 in tetrahydrofuran and 26 in acetonitrile [13] that can be used in a variety of base-catalyzed processes. However, given their

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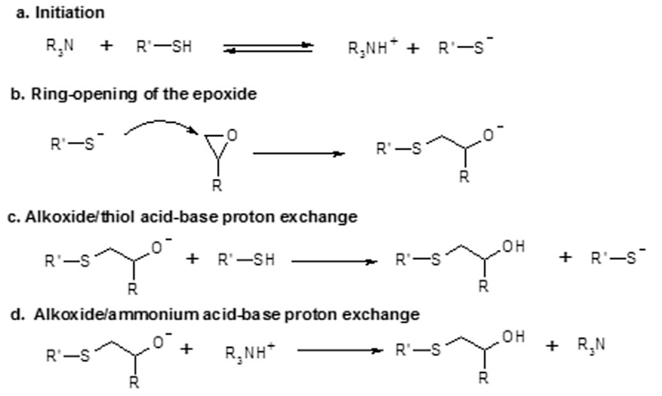
* Corresponding author.
E-mail address: osman.konuray@mmt.upc.edu (A.O. Konuray).

http://dx.doi.org/10.1016/j.polymer.2017.03.064



Scheme 1. Proposed curing mechanism for the base-catalyzed thiol-epoxy condensation.

low quantum yield and the limited absorption range (below 300 nm wavelength), tetraphenylborate PBs are commonly used in combination with photosensitizers such as isopropylthioxane (ITX) [8,9] in order to extend the absorption range towards longer wavelengths, up to the visible light range.

However, tetraphenyl borate amine salts can also be used as latent thermal catalysts. For instance, Kim and Chun [14] used commercially available 2,4-ethylmetylimidazole tetraphenylborate as catalyst for the reaction between naphthol and their epoxy derivatives, which can be catalyzed by bases such as imidazoles [15]. Therefore, for base-catalyzed reactions, tetraphenylborate ammonium salts have a dual photo-latent and thermally latent character that can be triggered with UV-light under mild temperature conditions or thermally activated where UV irradiation is not possible. This is an interesting feature which is also present in cationic catalysts such as diaryliodonium salts [16,17].

In this paper we study the applicability of TBD·$HBPh_4$ as thermally-latent and photolatent base for the curing of thiol-epoxy formulations based on diglycidyl ether of Bisphenol-A and pentaerythrithol tetrakis(3-mercaptopropionate) as crosslinking agent. The curing kinetics are analyzed using differential scanning calorimetry (DSC) and Fourier-transform infrared spectroscopy (FTIR). Model-free isoconversional methods and model-fitting methods are used to derive the kinetic parameters of the UV-activated or thermally-activated process. The storage stability of the materials are also analyzed.

2. Experimental

2.1. Materials

DGEBA with an epoxy equivalent weight of 187 g/eq (DG187, Epikote 828, Hexion Speciality Chemicals B.V.) was dried under vacuum prior to use. Pentaerythritol tetrakis (3-mercaptopropionate) (S4), triazabicyclodecene (TBD) and sodium tetraphenylborate ($NaBPh_4$) were supplied by Aldrich and used as received. Methanol (MeOH) and chloroform ($CHCl_3$) were supplied by VWR and used as received. Isopropylthioxane (ITX) was supplied by Ciba Specialty Chemicals Inc. and used as received.

TBD·$HBPh_4$ (PB hereafter) was synthesized using the procedure outlined in Ref. [13]. Firstly, TBD was solubilized in methanol (10 mmol in 10 mL MeOH) and slightly acidified with 36% HCl solution. $NaBPh_4$ was also solubilized in a small amount of MeOH and added with a slight excess to the acidified TBD solution. The formed salt was filtered, washed thoroughly with distilled water and MeOH, recrystallized from a 4:1 mixture of MeOH and $CHCl_3$, filtered and dried under mild heat and vacuum. To analyze its purity, its melting point was measured in a DSC thermal scan and was found to be identical to what is reported by Sun et al. [12].

Curing samples were prepared in 5 mL vials in 1–2 gr batches using the following procedure: PB was weighed and added to DG187 and was kept under agitation at 110 °C for 15 min. With this mixing procedure, an optimum balance between dispersion quality and latency is achieved. The mixture was left to cool down to room temperature after which S4 was added in a stoichiometric amount. To avoid premature activation, ITX was added lastly. The mixture was stirred continuously until homogeneous and subsequently analyzed. The samples not planned for immediate analysis were kept in a freezer at −20 °C. We coded our epoxy-thiol mixtures as *PBx UVy*, where x is the PB content in phr and is either 0.5, 1 or 2, and y indicates the duration (in minutes) of prior UV irradiation. Coding was done as *PBx noUV* for samples who were not UV irradiated. On the basis of previous works [9] the amount of ITX used was half the amount of PB in all formulations. The structures of the reagents used are shown in Scheme 2.

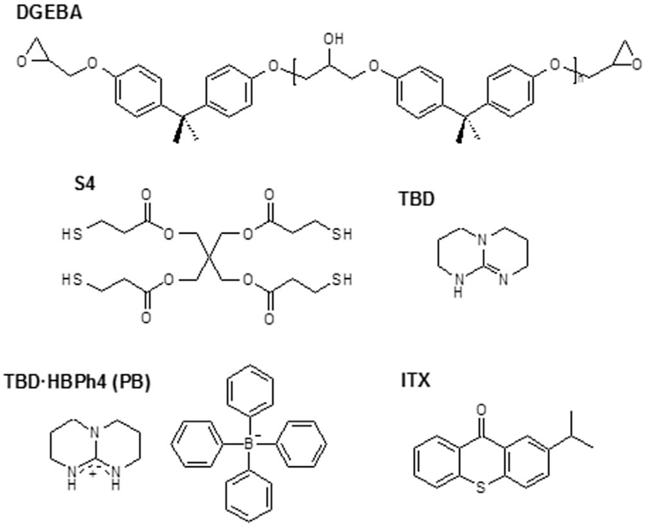
2.2. Fourier-transform infrared spectroscopy (FTIR)

We used a Brucker Vertex 70 FTIR spectrometer equipped with an attenuated total reflection (ATR) accessory (GoldenGate™, Specac Ltd.) which is temperature controlled in order to monitor the epoxy-thiol reaction and to verify the degree of cure of the samples. Spectra were collected in absorbance mode with a resolution of 4 cm^{-1} in the wavelength range from 4000 to 600 cm^{-1} averaging 20 scans for each spectrum. Scans were carried out every 60 s for a duration of time sufficient to observe the highest achievable conversion.

The absorbance peaks that we used to monitor conversion were 915 cm^{-1} and 2570 cm^{-1} for epoxy and thiol, respectively. These particular wavelengths have inherent complications such as overlaps resulting from the effect of different bonds [7]. As a result, they could only be analyzed qualitatively. We also monitored the hydroxyl band around 3500 cm^{-1} to confirm epoxy consumption.

2.3. Differential Scanning Calorimetry (DSC)

Calorimetric analyses of materials were carried out on a Mettler DSC822e thermal analyzer. UV irradiation of materials were



Scheme 2. Structures of the reagents used in this work.