Thermochimica Acta 519 (2011) 72–82

Contents lists available at ScienceDirect

Thermochimica Acta

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

Learning about novel amine-adduct curing agents for epoxy resins: Butyl-glycidylether-modified poly(propyleneimine) dendrimers

Jintao Wan[a,b], Zhi-Yang Bu[a], Cun-Jin Xu[a,c], Bo-Geng Li[a,*], Hong Fan[a,**]

[a] State Key Laboratory of Chemical Engineering, Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China
[b] Zhejiang Jiamin Plastics Co. Ltd., Jiaxing 314027, China
[c] Department of Chemistry and Chemical Engineering, College of Materials, Hangzhou Normal University, Hangzhou 310036, China

ARTICLE INFO

Article history:
Received 18 December 2010
Received in revised form 16 February 2011
Accepted 26 February 2011
Available online 21 March 2011

Keywords:
Poly(propyleneimine) dendrimers
Epoxy resin
Amine adducts
Nonisothermal reaction kinetics
Thermal stability
Dynamic mechanical properties

ABSTRACT

Novel butyl-glycidylether-modified poly(propyleneimine) dendrimers (PPIs) are prepared by reacting butyl glycidylether with PPI, which turn out to be able to cure bisphenol-A epoxy resin to an acceptable reaction extent. The nonisothermal reactions, dynamic mechanical properties and thermal stabilities of their cured epoxy resin are comparatively investigated with DSC, DMA and TGA, respectively. The model-fitting kinetic study demonstrates that Šesták–Berggren model can generally well simulate the reaction rates, and the isoconversional kinetic analysis with the Vyazovkin method indicates the curing agents, particularly their setric hindrance and the number of the –OH groups attached, greatly affect reaction kinetic schemes. Increasing the number of the BGE substituents attached to PPIs decreases the reactivity, glass- and beta-relaxation temperatures and thermal stability of the resulting epoxy systems, yet the intensity and width of the glass relaxation increase. This work offers a unique way of preparing modified-aliphatic-polyamine curing agents, and provides an opportunity to better learn about the amine-adduct curing agents which are widely used in room-temperature-cure epoxy coatings and adhesives from these good model compounds.

1. Introduction

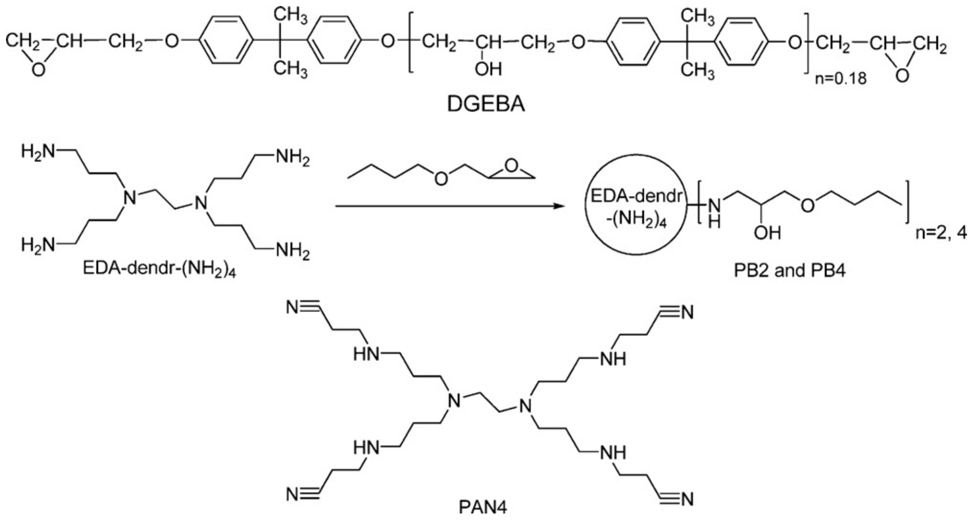
Epoxy resins are widely used in protective coatings, adhesives, sealants, filling materials, structural materials, advanced composites, modeling compounds for electronic encapsulation, electrical insulation materials and so forth for more than 60 years, because they have high mechanical strength, excellent chemical resistance, good electrical properties, low shrinkage, strong adhesion to many different substrates, and easy processing [1–3]. To obtain well-balanced final properties, they must be converted from oligomers or monomers of low molecular weights into a highly crosslinked network polymer in the presence of curing agents via a variety of reaction mechanisms [4]. Naturally, curing agents play a paramount role in determining curing conditions, processing and, particularly, end-use properties of epoxy resins, for which reasons they have being revived a lot of interests for many decades.

On the other hand, dendrimers [5–7] belong to well-defined highly branched molecules emanating from a central core with a large number of functional terminals at their periphery. Owing to their unusual chemical and physical properties such as the extraordinarily high functionalities, versatile tuneability, unique rheology properties, optical-enhancement effects, self-assembly, and host–guest particulates [8], dendrimers have been attracting tremendous interests in the recent 26 years since the first successful achievement of poly(amidoamine) dendrimers (PAMAMs) by Tomalia and co-workers [7]. Furthermore, some dendrimers have been shown the promising potentials in biomedicines [9], functional materials [10], catalysts [11], etc. Quite recently, a few preliminary attempts have been made to use dendrimers as the modifiers for thermoplastic polymers and the curing agents for thermosets. For example, Tande et al. [12] used ester-terminated poly(propyleneimine) dendrimers to plasticize polyvinyl chloride (PVC) with the decreased glass-transition temperature found, which is due to the additional free volume provided by the dendrimers. Other reports indicated that PAMAMs and these of similar molecular structures [13–17] could effectively crosslink epoxy resins. These dendrimers also exhibit the advantages of lowered vapor pressure, alleviated toxicity, reduced unfavorable odor, retarded carbonation in air, and improved compatibility with epoxy resins over the conventional linear-aliphatic-amine curing agents of low molecular weights (e.g., ethylenediamine). Unfortunately, PAMAMs and like-structure dendrimers tend to thermally degrade at a reactively low temperature (i.e., 120 °C for PAMAMs) [7], which even lowers than the curing temperatures (sometimes as high as 250 °C [18]) of most epoxy formulations, as a consequence of the

---

* Corresponding author. Tel.: +86 571 87952623; fax: +86 571 87951612.
** Corresponding author. Tel.: +86 571 87957371; fax: +86 571 87951612.
E-mail addresses: bgli@zju.edu.cn (B.-G. Li), hfan@zju.edu.cn (H. Fan).

0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.02.038



Scheme 1. Molecular structures of DGEBA, EDA-dendri-$(NH_2)_4$, PB2, PB4, PAN4, and epoxy resin (DGEBA).

retro-Michael addition of the weakened amidoamine linkages in their backbones [7]. This will adversely affect the curing reactions and further deteriorates the final properties of the epoxy resins.

Alternatively, amine-terminated poly(propyleneimine) dendrimers (PPIs) [19,20], consisting only of C–C and C–N linkages, take the advantages of excellent thermal stability (thermal decomposition temperature ≥300 °C [21]), lowered viscosity, and increased active-amine-hydrogen density over their PAMAM analogues. Thus, it is more promising for PPIs to serve as the curing agent for epoxy resins with improved properties. Furthermore, in principle it is also theoretically feasible to tailor the properties of the PPI-based epoxy curing agents such as compatibility, reactivity, pot life, crosslink density, flexibility, and solvent resistance via a number of chemical means to meet more specific requirements. In this respect, the chemical modification of PPIs may be a unique way to develop new curing agents with versatile properties. To the best of our knowledge, however, there are few fundamental and systematic studies on PPIs as the curing agents for epoxy resins to date [22–25], and in particular, there is a great demand for a better understanding of and reaching a deep insight into the effects of poly(propyleneimine) dendrimers and their modified products on the curing reactions and properties of epoxy resins. To this end, recently we have being performed a systematic study on this topic [23–25]. Our previous paper [23] focused on a novel curing agent for epoxy resins: the acrylonitrile-capped poly(propyleneimine) dendrimer (PAN4), see Scheme 1, which turned out to be able to well cure epoxy resins with the much decreased reactivity. The reason is that the electron-withdrawing acrylonitrile substituents on the amino functionalities lower the electron density on the resulting substituted-secondary amino groups, thus decreasing the nucleophilicity of the secondary amino functionalities.

As an extension of our previous work, this paper deals with novel curing agents for epoxy resins: butyl-glycidylether (BGE)-modified poly(propyleneimine) dendrimers (PB2 and PB4), with emphases on the nonisothermal reactions, dynamic mechanical properties, and thermal stability of the resulting epoxy resins. The primary objective of the present work is to clarify bonded BGE moieties, more bulk but less electron-withdrawing substituents (in fact slight electron-donating), on the properties of the resulting amine-adduct curing agents for epoxy resins. In industrial practices, BGE is frequently used to modify low-molecular-weight elementary polyamine curing agents to reduce their high volatilization and to improve other desired properties. This work will enrich our knowledge about the widely used but little fundamentally understood amine-adduct curing agents for epoxy resins [23,26], provide a better understanding of dendritic molecular architectures on the cure behaviors and properties of resulting epoxy systems, and further guide judicious molecular design and better applications of the new amine-adduct curing agents based on dendritic polyamines.

2. Experimental

2.1. Materials

Ethylenediamine (EDA) and acrylonitrile (Shanghai Reagent Co., Ltd., China) were purified by distillation prior to use. DGEBA, specific name: diglycidylether of bisphenol A (Heli Resin Co., Ltd., Suzhou, China), was dehydrated at 100 °C before use, with epoxide equivalent weight (EEW) of 196 g/eq. (data provided by the manufacturer). Butyl glycidylether, BGE (Huili Synthetic Materials Co., Ltd., Wuxi, China) was purified by distillation with an epoxy value of 0.695 mol/100 g. EDA-dendri-$(NH_2)_4$ (Scheme 1) was prepared in our lab with reference to published procedures [19,20].

2.2. Preparation of BGE-modified EDA-dendri-$(NH_2)_4$

The butyl-glycidylether-modified EDA-dendri-$(NH_2)_4$, PB2 and PB4 (Scheme 1), were prepared by reacting of BGE and EDA-dendri-$(NH_2)_4$ according to the mole ratio of epoxy to amine (N–H) = 1:2 for PB2 and 1:4 for PB4. To be more specific, BGE was added dropwise to continuously stirred EDA-dendri-$(NH_2)_4$ at 40 °C in 3 h according to the predesigned ratio, then the reaction mixture was heated to 50 °C, and held for additional 10 h. The final reaction product was discharged at room temperature to yield viscous colorless liquids (PB2 or PB4). The reactive hydrogen (N–H) equivalent weights of PB2 and PB4 were 94.5 and 215.5 g/eq., respectively.

2.3. Characterization

FTIR spectra of EDA-dendri-$(NH_2)_4$, PB2 and PB4 (thin films on KBr pallets) were recorded on a Nicolet^{TM} 5700 infrared spectrometer over the wavenumber of 4000–400 cm^{-1}.

Differential scanning calorimetry is the most convenient and powerful mean for studying highly exothermic reactions of epoxy resins due largely to its great accuracy and easy sample preparation [27]. Exotherms of the non-isothermal reactions as a function of time and temperature for DGEBA/EDA-dendri-$(NH_2)_4$, DGEBA/PB2, and DGEBA/PB4 were registered on a Perkin Elmer differential