Thermochimica Acta 623 (2016) 15–21

Contents lists available at ScienceDirect

Thermochimica Acta

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

Isothermal curing kinetics and mechanism of DGEBA epoxy resin with phthalide-containing aromatic diamine

Rong Ren [a], Xuhai Xiong [a,c,*], Xinghua Ma [a], Siyang Liu [b], Jing Wang [a], Ping Chen [b], You Zeng [c]

[a] Liaoning Key Laboratory of Advanced Polymer Matrix Composites, Shenyang Aerospace University, Shenyang 110136, China
[b] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China
[c] Shenyang National Laboratory for Materials Science, Advanced Carbon Division, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

ARTICLE INFO

Article history:
Received 1 September 2015
Received in revised form 3 November 2015
Accepted 7 November 2015
Available online 10 November 2015

Keywords:
Epoxy resin
Aromatic diamine
Curing kinetics
Isothermal DSC
Diffusion control

ABSTRACT

The curing reaction of diglycidyl ether of bisphenol A (DGEBA) with a novel aromatic diamine containing phthalide structure (BAPP) was studied by differential scanning calorimetery (DSC). The optimal formulation of DGEBA/BAPP system was obtained in terms of the curing behavior and glass transition temperature determined by dynamic DSC. The *n*th-order reaction model and autocatalytic model were used to analyze the curing kinetics and mechanism based on the isothermal DSC technique. The results indicated that the Kamal autocatalytic model had a great agreement with the experimental data from the start of curing reaction to the initiation of diffusion control stage. Diffusion-controlled effect was also taken into account and then the extended Kamal model could describe precisely the curing reaction of BAPP/DGEBA in the entire conversion range.

1. Introduction

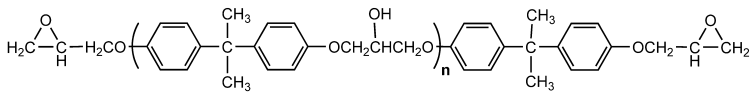
Epoxy resins are important and versatile thermosetting materials, which are effortlessly tailored to suit specific performance characteristics, and thus widely used in diverse industries spanned from electronic and electrical equipments to civil aviation and space parts as coatings, adhesives, electrical insulations, matrices for fibrous composites [1–4]. They could be cured by various types of hardener to obtain cross-linked network with mechanical properties ranging from extreme flexibility to high stiffness and strength [5–7]. Aromatic amine-cured epoxy systems enjoy more consideration and their applications are widened constantly in large load-bearing and harsh conditions due to their excellent corrosion and erosion resistance, high adhesive, good thermal stability and outstanding mechanical properties [6–9]. Unfortunately, those rigid materials also easily suffer from brittle fracture as a result of aromatic backbone and high cross-linked density. It is a focus of interest to obtain a balance between heat resistance and toughness of cured products by controlling microstructure of polymer network. A chain-extended aromatic amine with phthalide cardo structure was found to be an ideal candidate hardener for high-performance epoxy resins [10]. Its extended length of molecular chain could lead to an increase in the distance between the cross-linked points and then the toughness of epoxy network was improved. In the other hand, the introduction of heat-resistant multi-aryl skeleton might compensate for the loss of heat resistance resulting from decrease in the cross-linked density.

Generally, the low molecular weight linear liquid epoxy resin cannot meet end-use applications before it is converted to three-dimensional crosslinked network through curing process [11]. As curing reaction proceeds, the epoxy system will experience gelation and vitrification stages [9,12]. The crosslinked density increases and glass transition temperature (T_g) and mechanical properties are subsequently enhanced. For the epoxy/amine system, the curing reaction follows a complicated mechanism and many reactions occur, such as ring-opening reaction of the EP ring and primary amines for producing chain growth and secondary amines for building chain branches, etherification of EP ring with a pendant hydroxyl group and homopolymerization of EP group at higher temperature in the absence of active N—H functionality [3–5,13,14]. These necessitate the investigation on kinetic and mechanism of novel epoxy/amine system. Kinetic data can provide information for optimizing curing cycles to reduce manufacture cost or improve properties of cured products [5,8].

* Corresponding author at: Shenyang Aerospace University, Liaoning Key Laboratory of Advanced Polymer Matrix Composites, No.37 Daoyi South Avenue, Daoyi Development District, Shenyang, 110136, China. Tel.: +86 24 89723970.
E-mail address: xiongxuhai@sau.edu.cn (X. Xiong).

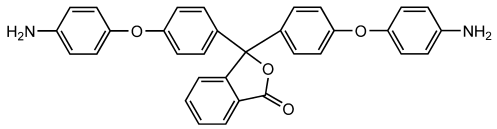
http://dx.doi.org/10.1016/j.tca.2015.11.011
0040-6031/

DGEBA



Diglycidyl ether of bisphenol-A

BAPP



3,3-Bis(4-(4-aminophenoxy)phenyl)phthalide

Scheme 1. Chemical structures of DGEBA and BAPP.

In our previous paper, we incorporated phthalide cardo structure into epoxy network by using a novel aromatic diamine containing phthalide structure (BAPP) as curing agent of diglycidylether of bisphenol A (DGEBA) epoxy resin [10]. The curing behavior and kinetics were investigated by differential scanning calorimetry (DSC) and the kinetic analysis of non-isothermal curing reaction showed that autocatalytic model was suitable to describe the curing mechanism. But it is actually rather difficult and unfaithful to recognize the reaction model type under non-isothermal conditions due to both rate constant, k, and reaction model vary simultaneously with temperature, giving rise to sigmoidal curves of the extent of conversion (α) versus temperature (T). On the contrary, autocatalytic profile is readily recognized based on isothermal data because in this case k = const, so that the kinetic curve shape is determined by the reaction model alone [15]. To continue previous study, isothermal DSC method was employed to investigate curing kinetics of DGEBA/BAPP system in the present paper.

2. Experiment

2.1. Materials

The epoxy compound used in the study was a diglycidylether of bisphenol A (DGEBA) provided from Wuxi Resin Works, with an epoxy equivalent weight (eew) of 185–210, and dried at 100 °C in vacuum for 1 h before use. The curing agent 3,3-Bis(4-(4-aminophenoxy)phenyl)phthalide (BAPP), was synthesized according to the published procedures [16]. The chemical structures of DGEBA and BAPP are shown in Scheme 1.

2.2. Preparation of DGEBA/BAPP blends

BAPP and DGEBA were completely mixed by mechanical stirring at 70 °C with BAPP/DGEBA stoichiometric ratios of 0.9, 1.0, 1.1, 1.2 and 1.3, respectively.

2.3. DSC characterization

To measure the total heat, ΔH_0, evolved during the complete cure, dynamic DSC analysis was performed under N_2 protection and run twice. The first scan was conducted from 30 °C to 300 °C at the heating rate of 10 °C/min to calculate ΔH_0, and the second scan was conducted from 30 to 200 °C at a heating rate of 20 °C/min to obtain the glass transition temperature (T_g).

To measure cumulative heat, ΔH_t, isothermal DSC analyses were carried out at 140 °C, 150 °C, 160 °C and 170 °C. And then the cured samples were also scanned from 30 to 200 °C at a heating rate of 20 °C/min to obtain T_g. The temperature and heat is calibrated with high-pure indium standard beforehand.

2.4. Fundamental theory on curing reaction kinetics of DGEBA/BAPP

The basic assumption for the application of DSC technique to the cure of the thermosetting polymers is that the reaction rate is considered to be directly proportional to the heat flow [9,13,17,18].

$$d\alpha/dt = (dH/dt)/\Delta H_0 = kf(\alpha) \quad (1)$$

where, $d\alpha/dt$ is the reaction rate, dH/dt is the heat flow, ΔH_0 is the overall reaction heat, k is specific rate constant at temperature T, $f(\alpha)$ is the reaction model and α is the extent of reaction, which is usually calculated by the following expression:

$$\alpha = \Delta H_t/\Delta H_0 \quad (2)$$

where, ΔH_t is the heat evolved up to a specific time. In this work, ΔH_t was calculated by integrating the isothermal DSC peaks up to a specific time and ΔH_0 was estimated by integrating the main exothermic peak of non-isothermal DSC curve measured at a heating rate of 10 °C/min.

The curing kinetics of epoxy/amine system has been frequently described by both nth order and autocatalytic mechanisms and $f(\alpha)$ is usually taken in the form of $(1-\alpha)^n$ or of $\alpha^m(1-\alpha)^n$, respectively [10,13]. For nth order kinetics, whose maximum reaction rate is at t = 0, $d\alpha/dt$ is proportional to the fraction of unreacted material and expressed as follow:

$$d\alpha/dt = k(1-\alpha)^n \quad (3)$$

where, n is the reaction order.

The characteristic of an autocatalytic kinetics is that the maximum rate of reaction is at some intermediate conversion, indicating that $d\alpha/dt$ is affected by unreacted material and resulted product. The Kamal model is a more conventional autocatalytic model: [17–22].

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1-\alpha)^n \quad (4)$$

where, k_1 and k_2 are the rate constants, and m and n are the kinetic exponents that depend on the nature of the epoxy resin and the amine hardener, and the curing temperature. Note that Eq. (4) is transformed into nth-order model. When m = 0.

Generally, reaction rate constant for curing reaction of thermosetting resin follows the Arrhenius law (Eq. (5)):

$$k = A\exp(-E/RT) \quad (5)$$

where, A is the pre-exponential factor, E is the activation energy, and R is the gas constant. Arrhenius parameters can be obtained from the temperature dependence of the rate constants k, k_1 and k_2.