



The curing kinetics and thermal properties of epoxy resins cured by aromatic diamine with hetero-cyclic side chain structure



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ABSTRACT

The use of novel aromatic diamine containing phthalide structure (BAPP) as curing agent of diglycidylether of bisphenol A (DGEBA) epoxy resin has been studied. BAPP can react with epoxy monomers by an epoxy-amine condensation mechanism, which renders phthalide cardo incorporate into the network structure of the thermoset. The curing behavior and kinetics have been investigated by differential scanning calorimetry (DSC) and the kinetic analysis of non-isothermal cure shows that autocatalytic model is suitable to describe the cure mechanism. The thermal–mechanical properties have been determined with dynamic mechanical analysis (DMA) and the activation energies for relaxation were calculated according to the Arrhenius law. Thermogravimetric analysis exhibits a lower initial decomposition temperature, decreased rate of decomposition and higher char yield compared with DGEBA cured with commercially available 4,4'-diaminodiphenylsulfone (DDS).

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1. Introduction

Curing agents play an important role in determining the practical use of epoxy resin [1–3]. The excellent properties, such as mechanical strength, heat resistance, durability and adhesiveness, are obtained by reacting the linear epoxy resin with suitable curatives to form three-dimensional crosslinked thermoset networks [4,5]. Therefore, design and development of novel curing agent is one of effective methods to improve properties of epoxy resin [2,5–8].

Despite the fact that epoxy resins could be cured by many types of hardeners, aromatic amines retain a prominent position in high-tech fields [9,10]. Epoxy resins cured with aromatic amine generally provide enhanced environmental (hydrolytic) stability, outstanding heat-resistant and mechanical properties [5,9]. 4,4'-diaminodiphenyl methane (DDM), *m*-phenylene diamine (*m*-PDA) and 4,4'-diaminodiphenylsulfone (DDS) are principal commercial aromatic-amine curing agents. These traditional aromatic amines with low molecular weight, however, bring on highly crosslinked materials, which are seized of greater brittleness. Generally,

increasing molecular chain of curing agent will reduce crosslinked density and further improve the toughness of network, but heat resistance is decreased [6]. Therefore, the chain-extended aromatic amines with multiaryl skeleton may provide a good balance between mechanical and thermal properties.

Phthalide moieties are the ever-popular hetero-cyclic side cardo groups and incorporated into polymer main chains to improve solubility, heat resistance and thermal oxidative stability [11–13]. Phenolphthalein and its derivations have been used largely as aromatic bisphenol monomers for preparing high-performance thermoplastics and thermosetting resins. Accordingly, phthalide-containing epoxy compounds were designed and synthesized, and various epoxy resin systems modified by polymers with phthalide cardo structure were developed [14–16]. Although phthalide-modified epoxy systems show a lot of advantages, a more cost-effective approach to introduce phthalide moiety into epoxy networks using phthalide-contained aromatic amine curing agents, which are of large molecular weight and have the potential to overcome the defects of traditional aromatic amines, has been not paid more attention.

The present work aims to investigate the curing kinetics and mechanism of diglycidylether of bisphenol A (DGEBA) epoxy resin cured with aromatic diamine containing phthalide structure (BAPP) by using the non-isothermal DSC. The thermal properties including thermal mechanical and thermal stability of cured material will be also studied by means of DMA and TGA.

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2. Experimental

2.1. Materials

Commercially available diglycidylether of bisphenol A (DGEBA)-based epoxy resin, with an epoxy equivalent of about 185–210 and average equivalent weight of 196, was supplied by Wuxi Resin Works, China, and dried at 100 °C in vacuum for 1 h before use. The hardener, 3,3-bis[4-(4-aminophenoxy)phenyl] phthalide (BAPP), was synthesized according to the reported method [17]. The molecular structures of chemical structures DGEBA and BAPP are illustrated in Scheme 1.

2.2. Preparation of DGEBA/BAPP blend

The prepolymer DGEBA/BAPP was prepared by mixing stoichiometric DGEBA and BAPP at 90 °C under vigorous mechanical stirring for about 5 min, and then a homogeneous, visually transparent mixture was obtained. The mixture was poured directly into preheated teflon mold and then the mold was transferred into an oven at 100 °C under vacuum for 5 min to drive off entrapped bubbles. The following temperature programs were used to finish the cure process in an air convection oven at 120 °C for 1 h, 160 °C for 2 h plus a post-cure period at 180 °C for 4 h. Finally, the casting was removed from the mold and characterized.

2.3. Characterization

Differential scanning calorimetry (DSC) measurements were conducted with a PerkinElmer Diamond DSC instrument. The DGEBA/BAPP mixture (about 7–9 mg mass) was loaded into sealed aluminum pan. All DSC experiments were performed under N₂ protection and run twice, the first scan was conducted from 25 to 300 °C at different heating rates of 5, 7.5, 10 or 15 °C/min and the second scan was conducted from 25 to 200 °C at a heating rates of 20 °C/min.

Dynamic mechanical analysis (DMA) was done on a TA Instruments Q800 DMA with an amplitude of 20 μm and a temperature ramp rate of 3 °C/min. The scanning temperature was from 25 to 200 °C and the driving frequencies were 1.0, 2.0, 5.0, 10 and 20 Hz. The cured DGEBA/BAPP specimens were cut to dimensions of 30 mm × 6 mm × 1 mm for the tension mode.

Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA-7 thermal analyzer and the cured DGEBA/BAPP sample (around 5 mg) was heated from 25 to 700 °C at a heating rate of 20 °C/min under the purified nitrogen flow rate of 60 mL/min.

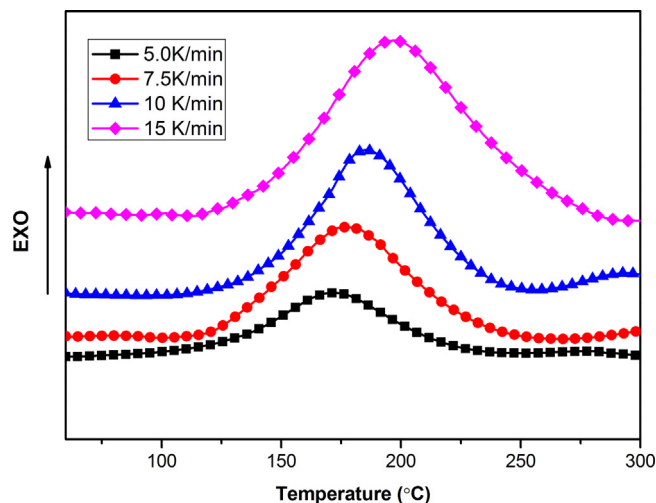


Fig. 1. Non-isothermal DSC thermographs of DGEBA/BAPP reactions.

3. Results and discussion

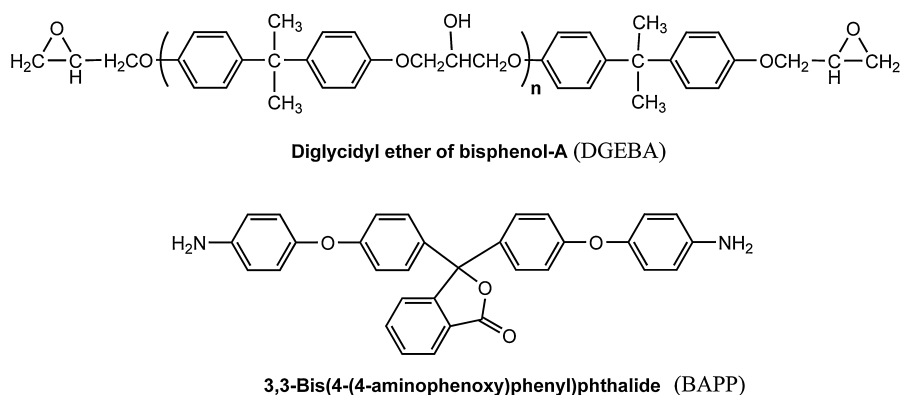
3.1. DSC analysis

3.1.1. Reactivity of DGEBA/BAPP

The non-isothermal curing reactions of DGEBA/BAPP were studied using DSC at a heating rate of 5, 7.5, 10 and 15 °C/min and the dynamic DSC thermograms and characteristic parameters are shown in Fig. 1 and Table 1, respectively. It can be seen that there is a single exothermic peak in each DSC curves and heating rate has a great influence on the shape of the exothermic curves. The exothermic peak is shifted to higher temperature and peak width is extended with increasing heating rate. In addition, the total heat release of cure reaction is independent of heating rate. In order to determine the glass transition temperature (T_g) of DGEBA/BAPP, the cured samples were carried out the second DSC test at a heating rate of 20 °C/min. As seen from Fig. 2, T_g value shows a strong dependence on the heating rate of the first DSC test and decreases by about 10 °C with shifting of heating rate from 5 to 15 °C/min (see Table 1). The believable cause is that the increasing heating rates reduce the network chains packing density, resulting in a decrease of steric hindrance to molecular motion.

3.1.2. Activation energy of the non-isothermal cure

The curing of epoxy resins is a multi-step chemical process that is complicated by the physical processes of gelation and vitrification [9,10]. Fortunately, the isoconversional analysis is a powerful



Scheme 1. Chemical structure of DGEBA and BAPP.

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