



Preparation, curing kinetic and properties of a novel amine with flexible polyoxypropylene side chain curing agent for epoxy resin



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ABSTRACT

A novel amine with flexible polyoxypropylene side chain (AFPE) was synthesized and characterized with FT-IR and NMR. Then, AFPEs with different molecular weight were used as a curing agent for diglycidyl ether of bisphenol A (DGEBA), and non-isothermal reaction was detected with DSC. The kinetic parameters of the curing process were determined by Málek method. A two-parameter (m , n) autocatalytic model (Šesták–Berggren equation) was found to be adequate to describe the reaction-controlled kinetics of the studied epoxy resins, yet was insufficient in depicting the diffusion-controlled kinetics of the epoxy resins. The values of E_a depended on the molecular weight of AFPEs, and increased with longer polyoxypropylene chain length in the AFPE. Dynamic mechanical analysis of AFPEs modified DGEBA/diethylenetriamine systems found that with the increasing molecular weight of AFPEs, α relaxation temperature, β relaxation temperature and crosslinking density decreased, while impact strength and elongation at break improved. From scanning electron microscope, tensile surfaces were rougher and sizes of cavities in the surface became larger with the increasing molecular weight of AFPEs. Our study showed that AFPE was a novel and effective toughening agent for epoxy resins.

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1. Introduction

Epoxy resins were found an extensive range of applications in protective coatings, adhesives, electronic-packaging materials and high-performance composites etc., due to good mechanical strength, outstanding chemical resistance, strong adhesion, superior dimensional stability, and wide formulation diversity [1–4]. However, the inherent brittle nature and poor crack resistance had greatly limited their applications. For recent years, numerous studies had been performed to toughen epoxy resins through the addition of flexible curing agents [5–7].

The most common method to enhance toughness of epoxy resins was to introduce a toughening agent, such as natural rubber [8–12] and thermoplastic modifier [13–16] etc. The phase separation of the second component from epoxy resin triggered extrinsic toughening that effectively retarded the crack tip and triggered plastic deformation, resulting in improving the fracture toughness of epoxy resins. During recent years, numerous efforts had been performed to introduce flexible chains into the structure of epoxy, such as polysiloxane [17–19], polyether [20,21] and epoxide soybean [22], etc. Through introducing flexible polyether chain to modify the epoxy backbone structure, crosslinking density of epoxy resin

decreased, resulting in decreasing tensile strength and Young's modulus, and increasing impact strength and elongation. Zhao et al. [21] showed that the insertion of n -alkylene group into the aminophenyl group of the amine terminated polyether slightly decreased the Young's modulus and tensile strength, and significantly increased the toughness and elongation. Yang et al. [5] used α,ω -amine terminated polyoxypropylene to toughen diethyl toluene diamine/diglycidyl ether of bisphenol A (DGEBA), and the results showed that tensile elongation at break and impact strength increased at both room temperature (RT) and 77 K. Ochi et al. [23] introduced alkyl side chain into cycloaliphatic epoxy resin, resulting in micro-phase separation structure and improving fracture toughness, when the side chain length reached $C_{10}H_{21}$.

In this paper, we prepared novel amines with different lengths of polyoxypropylene side chain (AFPE). Moreover, the curing kinetics of DGEBA-based epoxy resin with AFPEs were studied, and the effect of molecular weight of AFPEs on the network structures, morphologies and mechanical properties of the cured epoxy resins were also investigated.

2. Experimental

2.1. Materials

Diethylenetriamine (DETA, CP), methyl isobutyl ketone (MIBK, CP), toluene (CP), propylene oxide (CP) and potassium hydroxide

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(KOH, CP) were supplied from Shanghai Lingfeng Reagent Co., Ltd., and were used as received. 2,6-Butylated hydroxytoluene (99%, Aladdin) and diatomaceous earth (99%, Aladdin) were also used as received. Diglycidyl ether of bisphenol A (DGEBA) with the epoxide equivalent weight of 196 g/equiv. was kindly supplied from Shanghai Resin Co., Ltd., China.

2.2. Synthesis and characterization of ketimine

DETA (1 mol), MIBK (4 mol) and toluene (60 ml) were added into a three-neck round-bottom flask (1000 ml) equipped with a thermometer, Dean-Stark apparatus and mechanical stirrer, and stirred under argon. Then, the reaction mixture was heated to 110 °C until the water generated from the reaction mixture reached 36 ml. Finally, the unreacted methyl isobutyl ketone, toluene and remaining water were removed under vacuum to obtain ketimine and the yield was about 92%.

FT-IR spectrum of ketimine was recorded on a Nicolet 5700 infrared spectrometer over the wavenumber of 4000–400 cm^{-1} . Electrospray ionization mass spectrometry (ESI-MS) was recorded on a Micromass LCT mass instrument operating in the positive-ion mode.

2.3. Synthesis and characterization of AFPE

Ketimine (0.5 mol) as initiator, KOH (0.3 wt.%) and 2,6-butylated hydroxytoluene (0.1 wt.%) were added into a high-pressure autoclave (21) with digital control of stirring rate, and the temperature was heated to 100–130 °C under argon. Then stoichiometric propylene oxide (PO) was fed into the reactor slowly and the pressure in the reactor was kept at 0.3–0.5 MPa. After the feeding of PO was finished, the reaction was continued for 1 h at 110 °C. Then, the reaction mixture was cooled to room temperature, deionized water (3 mol) was added and the reaction mixture was heated to 100 °C for 4 h to hydrolyze imine completely. Finally, stoichiometric phosphoric acid and diatomaceous earth were charged to remove K^+ and decolor, followed by removing MIBK and excessive water, then filtered off the insoluble solid to achieve the liquid compound (AFPE) in bright yellow, and the yield was about 95%. The molecular weight of AFPEs was controlled through the molar ratio of PO and ketimine. The AFPEs were named as AFPE10, AFPE20, AFPE30 and AFPE40, respectively, and the number referred as the molar ratio of PO to ketimine. The synthesis route of ketimine and AFPE was listed in Scheme 1.

FT-IR spectra of AFPE were recorded on a Nicolet 5700 infrared spectrometer over the wavenumber of 4000–400 cm^{-1} . ^1H NMR (400 MHz) was detected in chloroform- d (CDCl_3) on an Ultra Shield 400 spectrometer (BRUKER BIOSPIN AG, Magnet System 400 MHz/

54 mm). Amine value was tested with hydrochloric acid–isopropanol method according to ASTM D2074–1992.

2.4. Curing kinetic of DGEBA/DETA and DGEBA/AFPEs

The non-isothermal reactions were recorded on DSC 2910 (TA Instruments) for multiple heating rates of 5, 10, 15 and 20 °C/min from 25 to 250 °C under nitrogen atmosphere of 20 ml/min. At first, the instrument was calibrated with purity indium standards at different heating rates. The DGEBA and relative amine curing agent at the stoichiometric ratio were mixed for 1 min under 300 r/min at room temperature. Then, the approximately 10 mg of the fresh mixture was enclosed in a DSC aluminum pan, and immediately subjected to a heating run.

2.5. Preparation and characterization of cured epoxy resins

As showed in Table 1, the stoichiometric DGEBA, DETA and AFPEs were stirred 2–3 min at 40 °C, degassed in vacuum, and poured into the preheated steel mold. The mixture was cured at 80 °C for 6 h and 120 °C for 12 h.

Dynamic mechanical properties of the cured epoxy specimens ($60 \times 10 \times 4 \text{ mm}^3$) were examined on Q800 (TA Instruments) at the heating rate of 5 °C/min from –100 °C to 250 °C in three-point bending mode with 1 Hz.

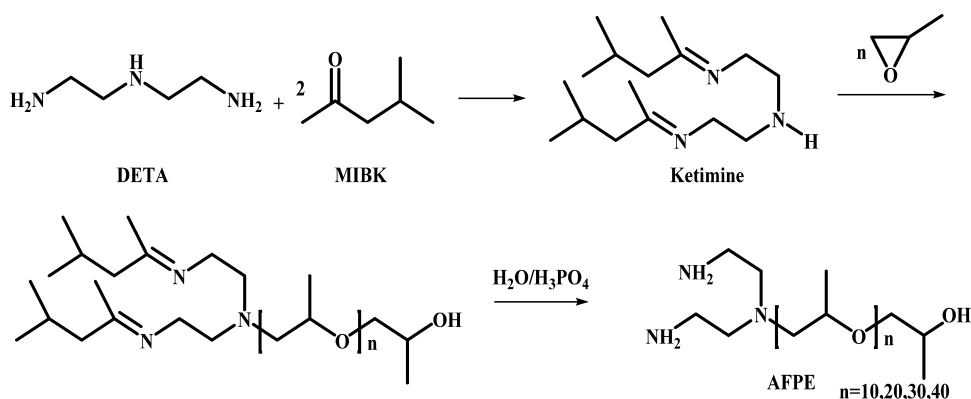
Surface morphologies of tensile fracture samples were recorded on an S-3400N SEM. The specimens were coated with a thin film of gold by sputtering.

Tensile test samples were performed on SANS tester under a 10 kN load cell with a crosshead speed of 5 mm/min at room temperature. The dumbbell specimens with a $115 \times 20 \times 4 \text{ mm}^3$ neck were used according to ASTM D638–2010. The bending samples ($80 \times 10 \times 4 \text{ mm}^3$) were tested according to ASTM D790–2003 using the same machine with a crosshead speed of 5 mm/min at room temperature. Impact samples ($80 \times 10 \times 4 \text{ mm}^3$) were tested on an impact tester (XCJ-4) according to GB/T 1043–2008.

3. Results and discussion

3.1. Structure of ketimine and AFPEs

The structure of ketimine was characterized by FT-IR and ESI-MS. Fig. 1 showed that the $\text{C}=\text{N}$ characteristic groups appeared at 1660 cm^{-1} , and the presence of absorptions at 3307 cm^{-1} and 1570 cm^{-1} were $\text{N}-\text{H}$ stretch vibration and scissor vibration, respectively. In Fig. 2, the molecular ion peak ($\text{M}+1$) at 268.1 was observed, which fitted well with the calculated value 268.



Scheme 1. Synthesis of ketimine and AFPE.

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