



Water resistance and curing kinetics of epoxy resins with a novel curing agent of biphenyl-containing amine synthesized by one-pot method



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ABSTRACT

In order to increase thermal stability and decrease water uptake of conventional epoxy resins, the biphenyl structure was introduced through the curing agent. A novel biphenyl-containing amine (BPDP) was synthesized by one-pot method and used as the curing agent for bisphenol-A epoxy resin DGEBA. Thermal property, water uptake and curing kinetics of the co-cured epoxy with diaminodiphenyl methane (DDM) were studied. The introduction of BPDP obviously improved the thermal stability, char yield, and water-uptake of the cured epoxy resins. The glass transition temperature T_g and weight-loss temperature increased with increasing BPDP content in the co-curing agent of BPDP and DDM. BPDP showed lower reactivity toward epoxy DGEBA than DDM with higher apparent activation energy E_a . Curing reaction of the epoxy resins co-cured with BPDP and DDM was investigated by non-isothermal DSC and the curing kinetics was described by a truncated two-parameter autocatalytic equation of the Šesták–Berggren model with experimentally determined parameters, which fitted the observed non-isothermal curing reaction rate quantitatively.

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1. Introduction

Epoxy resins have been widely used in adhesive, laminated composite, surface coating and semiconductor encapsulation due to the advantages in strong adhesive force to many substrates, excellent chemical resistance, mechanical and electrical performance, and thermal stability [1,2]. However, the conventional epoxy resins are unable to satisfy some application demands, such as integrated circuit package and advanced materials, which require high thermal resistance [3,4]. Hence, it is necessary to develop novel high heat resistant epoxy resin systems to meet these requirements.

Many efforts have been made to enhance the heat resistance of cured epoxy resins by changing chemical structure of the starting resins [5], which influences the property of final cured epoxy polymers. For example, the naphthalene-based epoxy resin was synthesized by introducing naphthyl and phenyl containing moieties. The cured naphthalene-cycloaliphatic epoxy resins showed high glass transition temperature T_g [6–8], which meant that the introduction of the rigid aromatic structure was an effective way to increase the thermal resistance. Liquid crystalline

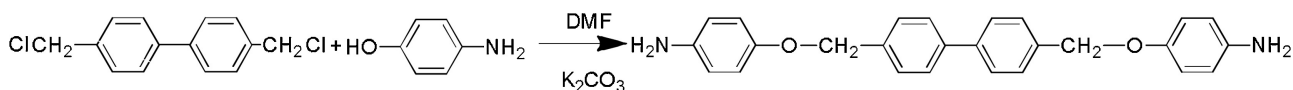
epoxy resins, especially based on the biphenyl mesogen, also exhibited a good thermal property [9–11]. To design and synthesize such epoxy resins containing the aromatic skeleton of large size by covalently bonding into the molecular backbone becomes the trend of recent studies [12,13]. Most strategies focused on preparing the epoxy resins with new biphenyl moieties, and the synthesis route was complicated with low yield of the final products [14–18]. Therefore, a convenient and facile way to produce biphenyl structure epoxy resins is expected.

On the other hand, curing agents affect not only the curing behavior of the epoxy resin, but also the physical properties of the final product. Along the approach to heat-resistant thermoset or composite, synthesis of novel curing agents containing rigid aromatic skeleton by convenient and facile method has been initiated in our group. Introduction of biphenyl structure into the curing agent backbone increases the rigidity of the cured epoxy resins, and the rigidity of the cured epoxy resins can be adjusted by the content of biphenyl structure curing agent. The heat-resistant property of the cured epoxy resins is desired to be improved in this way [9]. Furthermore, the water uptake of the cured epoxy resins can be effectively suppressed by introducing the biphenyl structure curing agent, which is very important for applications in the electric and electronic areas [6].

The information about the kinetics of curing reaction plays the key role in designing the curing formula and optimizing the curing

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Scheme 1. Synthesis of BPDP.

process [19]. So far, differential scanning calorimetry (DSC) has been widely used for kinetic study of the thermoset curing reactions with the basic assumption that the rate of heat released is proportional to the rate of the curing reaction [20]. Variety of kinetic models or methods have been proposed or employed to evaluate the kinetic parameters, such as the activation energy, pre-exponential factor, and reaction order. The experimentally determined parameters are then utilized in describing the kinetics mechanism and designing curing reactions [21–24].

In the present work, a novel curing agent of 4,4'-{[(1,1'-biphenyl)-4,4'-diylbis(methylene)]-bis(oxy)}dianiline (BPDP) was synthesized, using 4,4'-bis(chloromethyl)-1,1'-biphenyl and 4-aminophenol as the raw materials and potassium carbonate as catalyst by one-pot preparation. The non-isothermal curing kinetics of reaction with the epoxy resin diglycidyl ether of bisphenol-A (DGEBA) was investigated by DSC. The co-curing agent 4,4'-diaminodiphenylmethane (DDM) with similar primary amine group attaching to benzene ring was used to adjust the rigidity of the cured epoxy resin to observe changes in T_g , thermal stability, and water uptake.

2. Experimental

2.1. Synthesis of 4,4'-{[(1,1'-biphenyl)-4,4'-diylbis(methylene)]-bis(oxy)}dianiline

4-Aminophenol (12 g, 0.11 mol, Sigma–Aldrich), K_2CO_3 (18 g, 0.13 mol), and *N,N*-dimethyl formamide (DMF, 100 mL) were added into a 500 mL four-neck round bottom flask heated in an oil bath. The reaction mixture was stirred under nitrogen at 70 °C for 2 h for homogenization. Then, 4,4'-bis(chloromethyl)-1,1'-biphenyl (12.6 g, 0.05 mol, Shanghai Haoshen Co.) was added, and the reaction mixture was stirred under nitrogen at 80 °C for 4 h, followed at 90 °C for another 1 h. After the reaction was completed, the mixture was cooled down to room temperature, and DMF was removed by evaporation under reduced pressure. The obtained precipitate was washed with distilled water and ethanol, and then dried in vacuum for 48 h to obtain a powder product in brown color of 4,4'-{[(1,1'-biphenyl)-4,4'-diylbis(methylene)]-bis(oxy)}dianiline (BPDP) with a yield of about 90 wt% (Scheme 1).

FT-IR: 3421 cm^{-1} (N–H stretching), 3022 cm^{-1} (C–H stretching), 1651 cm^{-1} (C=C stretching), 1512 cm^{-1} (N–H bending), 1354 cm^{-1} (C–N stretching), 1226 cm^{-1} (Ar–O–C stretching), 812 cm^{-1} (C–H bending on benzene ring). ESI-MS: $m/z = 396$. 1H NMR: $\delta = 4.2$ – 4.6 (4H, amine), 6.4–6.7 (8H, phenylene), 7.3–7.6 (8H, biphenyl), 8.6 (4H, methylene). Elemental analysis for $C_{26}H_{24}N_2O_2$: Calc.% C: 78.27, H: 6.02, N: 6.84, O: 8.87; found % C: 78.78, H: 6.06, N: 7.07, O: 8.09.

Table 1
Formula of epoxy mixtures for curing.

Sample code	DGEBA (g)	BPDP (g)	DDM (g)
0BPDP	100	0	24
10BPDP	100	10	19.2
20BPDP	100	20	14.4
30BPDP	100	30	9.6
40BPDP	100	40	4.8
50BPDP	100	50	0

2.2. Curing of epoxy resin

Epoxy resin diglycidyl ether of bisphenol-A (DGEBA, E51 from Wuxi resin factory) with epoxy equivalent weight of 190 g/eq was mixed with curing agents 4,4'-diaminodiphenylmethane (DDM, Sinopharm Group Co.) and BPDP according to the stoichiometric ratio in Table 1, where the amount of the reactive group $-NH_2$ in DDM and BPDP was equal to that of the epoxy group in DGEBA. At first, BPDP and DDM were mixed in nitrogen atmosphere at 130 °C for 30 min, and then the homogenous liquid was cooled down to 90 °C. DGEBA was previously heated to 90 °C and added into the mixture of BPDP and DDM under rapidly stirring. The temperature of 90 °C was chosen to facilitate mixing and suppress the premature cure. After mixing, the homogenous mixture was rapidly cooled to room temperature to prevent the premature cure, casted into a mold, and degassed for 60 min in a vacuum chamber. The curing reaction was carried out at 100 °C, 120 °C, 150 °C, and 180 °C sequentially for 2 h each.

2.3. Characterization

1H NMR spectrum was recorded by a BrukerAvance-400 spectrometer using $CDCl_3$ or dimethyl sulfoxide ($DMSO-d_6$) as the solvent and tetramethylsilane (TMS) as the internal standard. Infrared spectrum was measured by a Nicolet 6700 Fourier transform infrared (FT-IR) spectrophotometer at room temperature using KBr pellet. Mass spectrum was obtained with an Agilent 1290 mass spectrometer. Elementary analysis was carried out on an Elementar Vario EL III.

A differential scanning calorimeter (DSC) of Netzsch 204 F1 was used to determine the conversion of curing reaction α and the glass transition temperature T_g of the cured epoxy resin under a nitrogen flow of 50 mL/min. ~5 mg of sample was sealed in an aluminum pan, and temperature was increased from 20 °C to 250 °C at heating rate of 2.5, 5, 10 and 15 °C/min, respectively. The midpoint between the onset and end of the inflectional tangent at the heat flow curve was taken as T_g . An empty pan was used as the reference and pure indium as the standard for calorimeter calibration.

Thermogravimetric analysis (TGA) was performed with a Netzsch TG 209 F3 thermogravimetric analyzer under N_2 atmosphere at a heating rate of 10 °C/min from 40 °C to 800 °C.

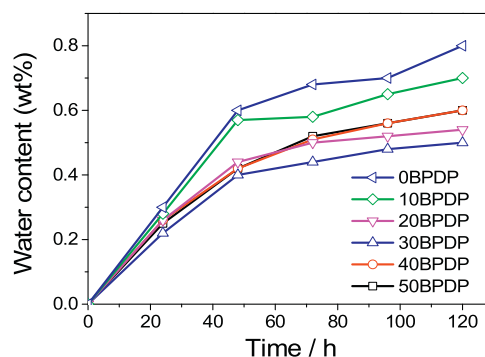


Fig. 1. Water uptake of cured epoxy resin with indicated BPDP content immersed in water at 30 °C.

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