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Thermal degradation kinetics and flame retardancy of phosphorus-containing dicyclopentadiene epoxy resins

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Abstract

The 2,6-dimethylphenol-dicyclopentadiene epoxy resin (MDE) was obtained by epoxidation of the intermediate 2,6-dimethylphenol-dicyclopentadiene novolac (MDN) which was synthesized from the reaction between dicyclopentadiene (DCPD) and 2,6-dimethylphenol. Subsequently, the 2,6-dimethylphenol-dicyclopentadiene advanced epoxy resin (MDAE) were prepared by reactions of 2-(6-oxido-6-H-dibenzo[c,e][1,2]oxaphosphorin-6-yl)-1,4-benzenediol (ODOPB) with MDE. The structure of MDN, MDE and ODOPB was confirmed by ^{1}H NMR, Fourier transform infrared (FTIR), elemental analyses (EA), mass spectroscopy (MS) and epoxy equivalent weight titration. Curing and thermal degradation kinetics of MDAE cured with diaminodiphenyl sulfone (DDS) were studied by the dynamic differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), respectively. The activation energies of dynamic curing and thermal degradation were calculated by using the Kissinger and Ozawa's methods, respectively. The dynamic model gives a good description of curing kinetics up to a much wider temperature range. The relations concerning the activation energy of curing and phosphorous content of epoxy resins were discussed. The char yields and thermal stabilities of cured ODOPB-modified epoxy networks uniquely increase with ODOPB contents. The degradation temperatures (T_d, 5%) in nitrogen at a heating rate of 20 °C/min ranged from 344 to 401 °C, and the char yields at 800 °C are 11–24%. The activation energies of degradation ranged from 190 to 268 kJ/mol. High LOI value (found 33.8) could be achieved with a low phosphorus content around 1.0%, which implied that the flame retardancy was improved by the incorporation of ODOPB.

Keywords: Dicyclopentadiene phosphorus-containing epoxy resin; Thermal degradation kinetics; Flame retardant; TGA

1. Introduction

Epoxy resins were used widely in the polymer industry for surface coatings, adhesives, painting materials, pottings, composites, laminates, encapsulants for semiconductors, and insulating materials for electric devices, etc. [1–10], because they have excellent fluidity, chemical resistance, low shrinkage on cure, superior electrical and mechanical properties, and good adhesion to many substrates. Several approaches for modification of the epoxy backbone to enhance the thermal properties of epoxy resins have been reported [11–13]. However, the thermal stability and flammability of common epoxy system are the major disadvantages in their applications. The epoxy resin in use is mainly the diglycidyl ether of bisphenol A (DGEBA) and the tetrabromobisphenol A (TBBA), however, the bromine-containing advanced epoxy resin release hydrogen bromide, dibenzo-*p*-dioxin and dibenzo-furan during combustion, which cause corrosion and toxicity. Organic phosphates do not cause any of these problems. Organophosphorus compounds have demonstrated better ability as flame retardants for polymeric materials by forming a carbonaceous char, which acts as a physical barrier to heat transfer from the flame to the polymer and diffusion of combustible gas and smoke than halogen-containing compounds [14–21]. Flame retardants, phosphorus–halogen

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mixtures, ammonium phosphate, and organophosphorus compounds have been used to impart flame retardancy to epoxy resins. Flame-retardant epoxy resins can be obtained by chemically bonding flame-retardant groups onto epoxy resins, and the permanent attachment of a flame retardant frequently leads to high efficiency in flame retardancy [22–24].

Hydrocarbon-containing epoxy resins, which were derived from the novolac of phenol and hydrocarbon in the presence of a Lewis acid, followed by epoxidization of the resulting hydrocarbon novolacs to epoxy resins. Among these hydrocarbons, dicyclopentadiene (DCPD) and higher oligomers of cyclopentadiene are the most commonly used starting materials because of their availability (DCPD is a by-product of C_5 streams in oil refineries), reactivity, and low cost. The structure of the 2,6-dimethylphenol–DCPD was introduced into the backbone to improve thermal property of the epoxy resins. In our laboratory, a rigid phosphorus-containing reactive 2-(6-oxido-6-H-dibenzo[c,e][1,2] oxaphosphorin-6-yl)-1,4-benzenediol (ODOPB) is synthesized and then incorporated to a 2,6-dimethylphenol-dicyclopentadiene epoxy resin, which is expected to exhibit the required flame retardancy, less fumes, and higher thermal stability than the conventional flame-retardant epoxy systems containing tetrabromobisphenol A. Kinetic characterization of thermosetting resins is the fundamental for understanding structure/property/processing relationships for manufacturing and utilization of high performance polymers. In this article, the effects of phosphorus contents on the thermal curing and thermal degradation behaviors of phosphorus-containing DCPD epoxy resins were studied by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) using dynamic experiments, respectively.

2. Experimental

2.1. Materials

Dicyclopentadiene (DCPD), 2,6-dimethylphenol, *p*-benzoquinone (BQ), and epichlorohydrin (ECH) were purchased from Acros. 4,4′-Diaminodiphenyl sulfone (DDS) was purchased from Chriskev. 9,10-Dihydro-oxa-10–phosphaphenanthrene 10-oxide (DOPO) from TCI and potassium hydroxide from Showa Co. were used as received. Ph_3P was triphenylphosphine, which was used as a curing accelerator. All solvents were commercial products (LC grade) and used without further purification.

2.2. Synthesis of 2,6-dimethylphenol–DCPD novolac (MDN) and its epoxy resin (MDE)

To a four-neck round-bottomed flask, equipped with a nitrogen inlet, stirrer, heating mantle, thermocouple, and temperature controller were added 2,6-dimethylphenol (1.42 mol) and $AlCl_3$ (0.03 mol). The reaction mixture was gradually heated to 120 °C, 0.2 mol of DCPD was added gradually over a period of 2 h, and the mixture was maintained at 120 °C for another 4 h. After the reaction was completed, 0.12 mol of 5 wt% aqueous sodium hydroxide was added, and the mixture was stirred for 1 h. The reaction mixture was filtered, and the filtrate was washed four times with deionized water. Next, the organic phase was separated and distilled in a rotary evaporator to remove excess 2,6-dimethylphenol. The crude products were dissolved in toluene and extracted with water for several times. The organic phase was distilled to remove toluene and water, and a deep-brown 2,6-dimethylphenol–DCPD novolac (MDN) was obtained in almost quantitative yield. The reaction scheme is shown in Scheme 1. MS (EI) *m/z* 376 (M+, 30); Elemental analyses for $C_{26}H_{32}O_2$: C = 82.90%, H = 8.60% (theoretically) and C = 82.59%, H = 8.63% (experimentally).

To a 1-L four-neck round-bottomed flask, equipped with a stirrer, heating mantle, thermocouple, temperature controller, and a Dean–Stark trap with a reflux condenser, were added 0.5 mol of the above synthesized MDN, 5 mol of ECH, and 80 g of the methyl ether of propylene glycol (1-methoxy-2-hydroxy propane) as a solvent. After stirring at room temperature and atmospheric pressure to thoroughly mix the contents, the temperature was raised to 65 °C and the pressure was reduced to 160 mm Hg absolute pressure. To the resultant solution was continuously added 42 g of a 40 wt% sodium hydroxide solution at a constant rate via a metering pump over a period of 3 h while maintaining the reaction temperature at 65 °C under a reduced pressure. During the addition of the NaOH solution, water was removed from the system by co-distilling with ECH and solvent; in the meantime distilled ECH and solvent were returned to the system. Upon completion of the addition, the reaction mixture was maintained at 65 °C for an additional 30 min. The resulting mixture was neutralized with a dilute aqueous potassium hydroxide solution and washed with deionized water. The organic phase was rotary evaporated at 180 °C under full vacuum over 3 h to remove the excess ECH and solvent. The residue was extracted with methyl isobutyl ketone (MIBK); the extract was washed four times with deionized water. The organic phase was separated and distilled to remove the solvents. A brown 2,6-dimethylphenol–DCPD epoxy resin (MDE) was obtained in almost quantitative yield (based on novolac). The reaction scheme is shown in Scheme 1.

2.3. Synthesis of ODOPB

To a 1-L four-neck round-bottomed reaction vessel equipped with a temperature controller, an overhead stirrer, and a reflux condenser were charged 500 g of ethoxyethanol and 270 g (1.25 mol) of DOPO; then, 122 g (1.13 mol) of powdered *p*-benzoquinone (BQ) was added incrementally. The temperature of the reaction mixture was raised to 125 °C, and the mixture was allowed to react at that temperature for 4 h. The resulted product was filtered and further recrystallized from ethoxyethanol to produce white solids. The yield of ODOPB is 97%, melting point of 254–256 °C (in Scheme 2). IR (KBr): 947 cm^{-1} (P–O–Ph), 1218 cm^{-1} (P═O), 3400 cm^{-1} (Ph–OH), 1580 cm^{-1} (P–Ph). MS (EI) *m/z* 324 (M+, 85); Elemental analyses for $C_{18}H_{13}O_4P$: C = 66.67%, H = 4.01%,