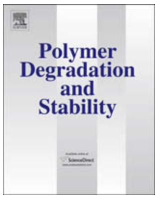
Polymer Degradation and Stability 94 (2009) 617–624

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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



Synthesis, characterization, thermal properties and flame retardancy of a novel nonflammable phosphazene-based epoxy resin

Ran Liu, Xiaodong Wang*

Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, School of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:
Received 18 November 2008
Received in revised form
2 January 2009
Accepted 9 January 2009
Available online 18 January 2009

Keywords:
Flame retardancy
Phosphazene
Epoxy resin
Synthesis
Thermal stability

ABSTRACT

Hexakis(4-hydroxyphenoxy)-cyclotriphosphazene (PN–OH) was synthesized through nucleophilic substitution of the chloride atoms of hexachlorocyclotriphosphazene and reduction of the aldehyde groups, and its chemical structure was characterized by elemental analysis, ^{1}H and ^{31}P NMR, and Fourier transform infrared (FTIR) spectroscopy. A new phosphazene-based epoxy resin (PN-EP) was successfully synthesized through the reaction between diglycidyl ether of bisphenol-A (DGEBA) and PN–OH, and its chemical structure was confirmed by FTIR and gel permeation chromatography. Four PN-EP thermosets were obtained by curing with 4,4′-diaminodiphenylmethane (DDM), dicyandiamide (DICY), novolak and pyromellitic dianhydride (PMDA). The reactivity of PN-EP with the four curing agents presents an increase in the order of DDM, PMDA, novolak and DICY. An investigation on their thermal properties shows that the PN-EP thermosets achieve higher glass-transition and decomposition temperatures in comparison with the corresponding DGEBA ones while their char yields increase significantly. The PN-EP thermosets also exhibit excellent flame retardancy. The thermosets with novolak, DICY and PMDA achieve the LOI values above 30 and flammability rating of UL94 V-0, whereas the one with DDM reaches the V-1 rating. The nonflammable halogen-free epoxy resin synthesized in this study has potential applications in electric and electronic fields in consideration of the environment and human health.

1. Introduction

Epoxy resins are widely applied as advanced composite matrices in electronic/electrical industries where a remarkable flame-retardant grade is required, but the fire risk is a major drawback of these materials [1]. There are two approaches to achieve flame retardancy for polymers generally known as the ‘‘addition’’ and the ‘‘reaction’’, and the latter is given much attention recently [2]. Traditionally, brominated reactive compounds [3] are used as co-monomers with epoxy resins to obtain fire-retardant materials. However, flame-retardant epoxy resins containing bromine can produce corrosive and obscuring smoke and may give super-toxic halogenated dibenzodioxins and dibenzofurans with deleterious effects on the environment and human health. Recently, in consideration of environmental problems, researches for halogen-free fire-retardant epoxy resins have received a great deal of attention [4,5]. Phosphorylation is considered to be one of the most efficient methods to confer flame retardancy on epoxy resins [6–8], whereas phosphate-based epoxy resins could possess excellent flame retardancy only when using amine curing agents. Some studies indicated that the flame-retardant efficiency significantly improved when phosphorus and nitrogen existed simultaneously in the curing system of epoxy resin. Therefore, the phosphorus–nitrogen synergistic effect on flame retardancy is very interesting [9].

In recent years, there has been considerable interest in the phosphazene-based family of materials because they not only have a wide range of thermal and chemical stabilities, but also can provide improved thermal and flame-retardant properties to polymers and their composites [10–15]. Hexachlorocyclotriphosphazene is a versatile starting oligomer for the synthesis of phosphazene-based polymers. The chlorine groups attached to the phosphorus atoms are easily substituted by various nucleophiles to form reactive cyclotriphosphazenes. Cyclotriphosphazene, as a ring compound consisting of alternating phosphorus and nitrogen atoms with two substituents attached to the phosphorus atoms, exhibits unusual thermal properties such as flame retardancy and self-extinguishability [16,17]. Cyclotriphosphazene has several advantages as a reactive flame-retardant functional oligomer. First, the flexible synthetic methodology can be developed for preparation of cyclotriphosphazene-based copolymer with various substituents, which allows us to obtain multifunctional initiators or terminators with ease. Second, thermal and nonflammable properties of the

---

* Corresponding author. Tel.: +86 10 6441 0145; fax: +86 10 6442 1693.
E-mail address: wangxdfox@yahoo.com.cn (X. Wang).

0141-3910/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2009.01.008

cyclotriphosphazene moieties can be conferred to the resulting polymers, especially, of low molecular weights [12,13,18–20]. Therefore, when cyclotriphosphazenes are incorporated into the network of thermoset polymers, they can increase the thermal property and flame retardancy of the polymers because of phosphorous and nitrogen flame-retardant synergy. The reason is that the thermal decomposition of the phosphazene-based polymers is an endothermic process, and phosphate, metaphosphate, polyphosphate generated in the thermal decomposition form a nonvolatile protective film on the surface of the polymer to isolate it from the air; meanwhile, the inflammable gases released such as CO_2, NH_3 and N_2 cut off the supply of oxygen so as to achieve the aims of synergistic flame retardancy [21–24]. The phosphazene-based polymers have more effective flame retardancy than any other flame-retardants, making them a new focus [25–29]. However, the phosphazene-based polymers used as a flame-retardant component with epoxy resins are seldom reported [28]. In this study, we developed a novel nonflammable halogen-free epoxy resin by incorporating the cyclotriphosphazene group, and investigated the thermal property and flame retardancy of this thermoset resin with various curing agents.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) was purchased from Shanghai Jiachen Chemical Co. Ltd., China. The epoxy resin (diglycidyl ether of bisphenol-A, DGEBA) with an epoxide equivalent weight (EEW) of 184–194 g/equiv. was kindly supplied by Wuxi Bluestar Epoxy Co., China. Triphenylphosphine, sodium hydride (NaH), sodium borohydride ($NaBH_4$), 4-hydroxybenzaldehyde, tetrahydrofuran (THF), acetone, 4,4′-diaminodiphenylmethane (DDM), pyromellitic dianhydride (PMDA), dicyandiamide (DICY) and novolak were purchased from Beijing Chemical Reagent Co., China.

2.2. Synthesis of hexakis(4-aldehydephenoxy)-cyclotriphosphazene

A suspension of sodium 4-aldehydephenoxide in dry THF was prepared by mixing 274 g NaH (70 wt.% diluted in oil) and a solution of 976 g 4-hydroxybenzaldehyde in 500 mL THF in a reactor with mechanical stirring, reflux condensation and a nitrogen inlet. Subsequently, 348 g $N_3P_3Cl_6$ was dissolved in 400 mL THF and added dropwise into the flask over a period of 60 min, and then the reaction system was maintained at 65 °C for 48 h. Some light-brown powders as hexakis(4-aldehydephenoxy)-cyclotriphosphazene (PN–CHO) were collected after recrystallization with ethyl acetate, and the yield was 72.6 wt.%.

2.3. Synthesis of hexakis(4-hydroxyphenoxy)-cyclotriphosphazene

$NaBH_4$ (56 g) was added into a reactor containing a solution of 200 g PN–CHO in 500 mL THF/methanol mixture. The reaction system was stirred at room temperature for 14 h. Some white solids as hexakis(4-hydroxyphenoxy)-cyclotriphosphazene (PN–OH) were obtained after recrystallization with 90 vol.% alcohol, and the yield was 81.3 wt.%.

2.4. Synthesis of phosphazene-based epoxy resins

DEGBA (1000 g) was added into a reactor and stirred for 2 h at the temperature of 120 °C under a nitrogen atmosphere, and then 318 g PN–OH with the equivalent ratio to DGEBA of 1:14 and appropriate amount of triphenlyphosphine (0.3 wt.%) as a catalyst were added. The reaction mixture was maintained at 175 °C for 5 h. And some light-yellow gel-like phosphazene-based epoxy resin (PN-EP) was obtained with a yield of 86.4%.

2.5. Curing procedure of the PN-EP

The synthesized PN-EP and DGEBA as a control were cured using 4,4′-diaminodiphenylmethane (DDM), dicyandiamide (DICY), novolak and pyromellitic dianhydride (PMDA) as curing agents. The epoxy resin was dissolved in appropriate amount of acetone, and then the curing agent with an equivalent ratio to PN-EP of 1:1 and 2-methylimidazole (0.2 wt.%) as a curing accelerator were added into this solution. The mixture was stirred constantly to be a homogeneous solution and then was kept in a vacuum oven at 50 °C for 1 h to remove the solvent. The curing process was carried out in terms of the curing conditions determined by the DSC tracings of the respective curing systems as listed in Table 1. In the end of the curing procedure, the cured system was cooled gradually to room temperature to avoid stress crack.

2.6. Characterization

Elemental analysis was carried out using a Heraeus CHN-O rapid elemental analyzer with acetanilide as a standard. ^1H and ^{31}P nuclear magnetic resonance (NMR) spectra were obtained by a Bruker AV-600 NMR spectrometer at 300 MHz using dimethyl sulfoxide (DMSO)/D_2O as solvent with tetramethylsilane and phosphoric acid as external standards, respectively. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 205 FTIR spectrometer with the scanning number of 30. EEWs of the synthesized PN-EPs were measured by HCl/acetone chemical titration method. Gel permeation chromatography (GPC) was performed by a Waters 515 GPC with THF as a solvent at a flow rate of 1.0 mL/min. The number average molecular weights (M_n) and weight average molecular weights (M_w) were obtained from the analysis of the GPC data.

The curing systems of PN-EPs with various curing agents and the glass-transition temperature (T_g) of the cured samples were determined using a TA instrument Q100 differential scanning calorimeter (DSC) under a N_2 atmosphere at a heating rate of 10 °C/min with the sample weights about 10 mg. Thermogravimetric analysis (TGA) was carried out on a TA instrument Q50 thermal gravimetric analyzer at a heating rate of 10 °C/min from 50 to 600 °C under a N_2 atmosphere. UL94 horizontal and vertical burning tests were carried out in terms of the method proposed by Underwriter Laboratory. Three horizontally clipped samples (127 × 12.7 × 1.6 mm) were ignited by a butane burner with a butane flow of 105 mL/min. The samples would achieve the flammability rating of UL94 HB if the burning speed was less than 75 mm/min and each of them extinct before it reached 100 mm. Five samples hung vertically over some surgical cotton were ignited by the butane burner with the same flow. The samples would achieve the UL94 V-0 flammability rating if the combustion of each sample did not last for 10 s and the cotton below the tested sample could not be ignited by the sparks. Limiting oxygen index (LOI) measurement was performed using a HD-2 oxygen index apparatus with a magneto-dynamic oxygen analyzer according to ASTMD D-2863. The sample (65 × 3.0 × 0.5) was

Table 1
Curing programs of PN-EP cured with various curing agents.

Curing system	Curing temperature (°C)	Curing time (min)	Postcuring temperature (°C)	Postcuring time (min)
PN-EP/DDM	120	60	150	180
PN-EP/DICY	160	30	190	60
PN-EP/novolak	140	60	170	180
PN-EP/PMDA	180	60	200	180