



Synthesis of a novel linear polyphosphazene-based epoxy resin and its application in halogen-free flame-resistant thermosetting systems



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ABSTRACT

The synthesis of a novel linear polyphosphazene-based epoxy resin (LPN-EP) was performed via a six-step reaction pathway, and the chemical structures of the intermediate and target products were characterized by ^1H and ^{31}P NMR spectroscopy and Fourier transform infrared spectroscopy. A series of thermosetting systems consisting of diglycidyl ether of bisphenol-A and LPN-EP were prepared, and their mechanical properties, thermal stabilities, and flame retardant properties were investigated. The resulting thermosets exhibited excellent flame resistance with the UL-94 V-0 rating but also achieved a significant improvement in impact toughness as a result of the incorporation of rubbery LPN-EP. The thermosets also showed a good thermal stability highlighted for high char yields. The mechanism study indicates that the synergistic effect from the combination of phosphorus and nitrogen in polyphosphazene segments could effectively enhance the flame retardancy by acting in both condensed and gaseous phases to promote the formation of intumescent phosphorus-rich char on the surface of the thermosets. Such a char layer plays a role of insulating protective shell to prevent the volatiles from transferring to the surface of the thermosets as well as to shield the heat and oxygen diffusion, thus resulting in a self-extinguishing flame rating.

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1. Introduction

There is a greatly concern about the emission of hazardous substances and the resulting environmental pollution with an increasing demand for new fire-resistant materials for the industrial and civil applications. As one of the most important functional materials with immanent flame retardancy, the brominated epoxy resin has been widely used for the electronic and electrical manufactures because of its outstanding characteristics such as high mechanical strength, good thermal and chemical stabilities, high flame resistance up to UL-94 V-0 rating, superior electrical insulating performance, and low shrinkage on cure [1–3]. Although such a traditional flame-retardant epoxy resin was well developed to meet the considerable secure requirements against the fire hazard, it unfortunately generated an environmental impact because of the production of super toxic brominated dibenzodioxins and dibenzofurans during combustion [4,5]. These

halogenated substances with potential carcinogenicity not only are very harmful to human health but also bring pollution disasters when released into the environment [6,7]. In recent years, the use of halogen-containing materials in electrical appliances and electronic equipments has been legislatively restricted by the European Union according to the Restriction of Hazardous Substances (RoHS), and some of the brominated flame retardants were banned from the European Union market. Meanwhile, the World Health Organization and the US Environmental Protection Agency also recommended exposure limits and risk assessment of halogenous compounds to promise meeting the global sustainable development goals [8,9]. Therefore, the research and development of halogen-free fire-resistant epoxy resin have been attracting the increasing attention from both the scientific and industrial communities.

The design and synthesis of the epoxy resins containing phosphorus- or nitrogen-containing or both were considered as an effective pathway to gain flame retardancy for the resultant polymers as well as to avoid the use of halogenated components [10–12]. In past decades, many studies declared the realization of such a strategy through tailoring the epoxy-based macromolecules from backbones to side groups by incorporation of

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phosphine oxide, phosphates, and the other phosphorylated and phosphonylated derivatives [13–18], because organophosphorus moieties are efficient radical scavengers and flame quenching agents. These studies also indicated that the combination of phosphorus-containing epoxy resins and nitrogen-based hardeners could lead to a dramatically high flame-resistant efficiency due to the phosphorus–nitrogen synergistic effect based on a condensed-phase mechanism involving polymer charring and a gaseous-phase flame-inhibition mechanism by removing the heat and diluting the combustible materials during fire process [19–24]. There is no doubt that the synthesis of reactive flame-retardant polymers can provide permanent flame retardancy for the epoxy curing system as well as maintains the original physical properties in a better way [13,19]. However, these phosphorus-containing epoxy systems hardly gain a high weight fraction of phosphorus, resulting in a low degree of flame retardancy [25,26]. There is still a challenge involving the achievement of high mechanical performance and effective flame retardancy at the same time. Therefore, the increasing focus on these issues has drawn the attention to the redesign of the epoxy macromolecules with more effective flame retardancy as well as better mechanical properties.

The epoxy resins containing cyclotriphosphazene group have recently attracted a great interest. It is well known that the phosphazenes present the alternating phosphorus and nitrogen atoms in a conjugative mode [27,28]. Such a unique chemical structure offers the synergism of the phosphorus–nitrogen combination resulting in outstanding flame retardancy and thus causes the originally highly flammable organic materials with auto-extinguishing [29,30]. This feature makes phosphazenes particularly good candidates as the flame-retardant materials for electric and electronic applications. A literature survey indicates that there are several investigations focused on the design and synthesis of the flame-retardant epoxy polymers with cyclotriphosphazene moieties in star-like, cycloliner, spirocyclic, and cyclomatrix structures [31–35]. Nevertheless, the chemical incorporation of cyclotriphosphazene rings into the epoxy resins hardly achieved a high phosphorus/nitrogen content because of their steric effect, which may also lead to a high brittle nature of the resultant polymers [36]. The goal of this work is to design a novel epoxy curing system containing linear polyphosphazene moieties for halogen-free flame resistance. The linear polyphosphazene segment not only has the high phosphorus/nitrogen content resulting in excellent flame retardancy but also can generate a toughening effect for the resultant epoxy thermosets due to its rubbery nature. The synthesis and characterizations of the intermediate and final products were described, and the non-isothermal curing behaviors, mechanical performance, thermal stability and flammability characteristics of this epoxy systems was also investigated.

2. Experimental section

2.1. Chemicals

Phosphorus pentachloride (PCl_5), ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$], 4-hydroxybenzaldehyde, sodium hydride (NaH , 70% suspension in mineral oil), phenol, sodium borohydride (NaBH_4), hexadecyl trimethyl ammonium bromide (CTAB), epichlorohydrin, 4,4'-Diamino-diphenylmethane (DDM), tetrahydrofuran (THF), tetrachloroethane (TCE), methyl alcohol (MA), and *n*-hexane were all purchased from Beijing Chemical Reagent Co., Ltd., China. Diglycidyl ether of bisphenol-A (DGEBA) with an epoxy equivalent weight (EEW) of 187 g/equiv. was kindly provided by Wuxi Resin Factory of BlueStar New Chemical Materials

Co., Ltd., China. The solvent, THF, was distilled from sodium benzophenone ketal prior to use, and the other chemicals and reagents were used as received.

2.2. Synthesis and reactions

The linear polyphosphazene-based epoxy resin (LPN-EP) was synthesized via six-stage reactions. In a typical process: a 1000-mL four-neck round-bottom flask equipped with a thermometer, a reflux condenser, a nitrogen inlet, and a mechanical stirrer was charged with 440 mL of TCE, 166.4 g of PCl_5 , and 21.6 g of $(\text{NH}_4)_2\text{SO}_4$, and the mixture was heated to 145 °C with stirring for 1.5 h. After the reaction was completed, the reactant mixture was filtered, and the solvent was removed on a reduced pressure rotary evaporator, leaving a colorless oil of *N*-(dichlorophosphoryl)-*P*-trichloromonophosphazene (87.48 g, yield 99.4%) as product **1**.

The product **1** was added into a three-neck round-bottom flask to perform polymerization at 245 °C for 2 h under a nitrogen atmosphere. A dark brown rubbery poly(dichlorophosphazene) as product **2** was obtained after removing by-products. The product **2** (40.0 g) was dissolved in 500 mL of THF to form a clear solution, and then sodium 4-formylphenolate (19.88 g) obtained from the reaction of 4-hydroxybenzaldehyde with NaH was added to this solution to perform a reaction at 65 °C for 6 h under a nitrogen atmosphere. Then, the reactant mixture was filtered, and the solvent was removed on a reduced pressure rotary evaporator, leaving a brown rubbery polymer of $[\text{NP}(\text{OC}_6\text{H}_4\text{CHO})\text{Cl}]_{0.4}(\text{NPCl}_2)_{0.6}]_n$ as product **3**. In succession, the product **3** (51.8 g) was dissolved in 500 mL of THF, and then sodium phenoxide was added into this solution to perform a reaction at 70 °C for 24 h. After the reaction was completed, the resultant mixture was filtered, washed repeatedly with the aqueous solution of NaHCO_3 and hot water, and then dried with anhydrous Na_2SO_4 . After the solvent was removed by rotatory evaporation under reduced pressure, a off-white rubbery polymer of $[\text{NP}(\text{OC}_6\text{H}_4\text{CHO})(\text{OPh})]_{0.4}(\text{NP}(\text{OPh})_2)_{0.6}]_n$ as product **4** was obtained.

The product **4** (40.0 g) was dissolved in 500 mL of THF/methanol (1:1) mixture, and then 2.6 g of NaBH_4 was added. The reaction suspension was stirred at room temperature for 24 h. After the reaction was completed, the solvent was removed by rotatory evaporation, and then the resultant suspension was filtered, washed repeatedly with hot water, and then dried with anhydrous Na_2SO_4 . After the solvent was removed by rotatory evaporation under reduced pressure, a off-white rubbery polymer of $[(\text{NP}(\text{OC}_6\text{H}_4\text{CH}_2\text{OH})(\text{OPh}))_{0.4}(\text{NP}(\text{OPh})_2)_{0.6}]_n$ was obtained as product **5**. A 500-mL three-neck round-bottom flask equipped with a mechanical stirrer, a reflux condenser, and a nitrogen inlet was charged with 99.9 mL of epichlorohydrin, 75.0 g of product **5**, and 1.9 g of CTAB as a catalyst. The mixture was heated to 70 °C with stirring for 3 h, and then an aqueous solution of NaOH (12.6 mL, 40 wt.%) was added. The reaction was continuously performed with stirring at 85 °C for 3 h. After the reaction was completed, the rotatory evaporation was performed under reduced pressure to remove the solvents and unreacted reagents. The resultant mixture was washed repeatedly with hot water, filtered, and then dried under vacuum. Finally, a light yellow solid was obtained as LPN-EP.

2.3. Preparation of thermosetting systems

A conventional epoxy resin (DGEBA) was homogeneously mixed with different loadings of LPN-EP in THF at room temperature, and then DDM as a hardener was added according to a stoichiometric amount of 1:1 for epoxy curing systems. 2,4,6-Tris(dimethylaminomethyl) phenol (0.3 wt.%) as a curing accelerator was also added into the curing system. The resultant mixtures were kept in a

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