



Preparation, isothermal kinetics, and performance of a novel epoxy thermosetting system based on phosphazene-cyclomatrix network for halogen-free flame retardancy and high thermal stability



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ABSTRACT

A novel epoxy thermosetting system based on a phosphazene-cyclomatrix network was designed and successfully prepared through the crosslinking reaction of diglycidyl ether of bisphenol-A with trispiro(ethylenediamino)-cyclotriphosphazene. The study of isothermal crosslinking kinetics indicated that the crosslinking process could be simulated by the Kamal's model. The resultant thermosets exhibit excellent flame-retardant properties with a UL94 V-0 flame rating due to the presence of phosphazene-cyclomatrix network, whereas they show a higher thermal stability than the conventional epoxy thermoset. The mechanism study indicated that the phosphazene-cyclomatrix moieties could effectively enhance the flame retardancy by acting in both condensed and gaseous phases to promote the formation of an intumescent phosphorus-rich carbonaceous char layer on the surface of material. Such a char layer could prevent the volatiles from transferring to the surface of the thermosets as well as to shield the heat and oxygen diffusion, thus resulting in the self-extinguishing flame rating.

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1. Introduction

Cured epoxy resins are the most important thermosetting polymers known for their excellent adhesion, chemical and heat resistance, excellent mechanical properties, and very good electrical insulating properties, and they have achieved the extensive applications for paints coatings, adhesives, industrial tooling and composite materials such as those using carbon fiber and fiber glass reinforcements, electrical systems and electronics, etc. [1–4]. Nevertheless, like many other organic polymers, one of the main drawbacks of epoxy resins is their inherent flammability, which evidently restricts their applications in many areas with flame resistance required. The electronic and microelectronic industries are an up and coming area, in which epoxy resins have been playing a great role and are widely used as the primary resins for making printed circuit boards, overmolding integrated circuits, transistors and hybrid circuits, packaging semiconductor chips and devices, potting transformers, inductors and light-emitting diodes, and many more [5,6]. The fire safety is especially considered when epoxy resins are involved in these applications. Therefore, the

epoxy resins with excellent flame resistance as well as high performance have necessarily been required to avoid the fire risks. There is no doubt that the brominated epoxy resins have been well developed to meet the considerable secure requirements for the electronic and microelectronic manufactures because of their outstanding characteristics such as good thermal and chemical stabilities, excellent fire resistance up to the V-0 flame rating of UL94 classification, superior electrical insulating performance, and low shrinkage on cure [7]. However, the use of the brominated epoxy resins inevitably brought an environmental impact due to the release of super toxic brominated dibenzodioxins and dibenzofurans during combustion [8]. These halogenated substances with potential carcinogenicity are not only very harmful to human health but also bring pollution disasters when released into the environment [9]. Regardless of the end use, there are increasingly stricter standards and regulations (both national and international) governing the electric chemicals and materials to ensure the safe operation throughout the product lifetime. For example, the use of halogen-containing materials in electrical appliances and electronic equipments was 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

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halogenous compounds to promise meeting the global sustainable development goals [10,11]. In this case, the research and development of halogen-free flame-retardant epoxy resins have been attracting great attention from both scientific and industrial communities.

There have many methods, which have been developed to enhance the flame resistance of epoxy resins in the absence of the halogenated substances, and the design of the epoxy resins containing phosphorus- or nitrogen-containing or both are considered as an effective route according to a literature survey [12–14]. Such a strategy could be realized by tailoring the epoxy-based macromolecules from backbones to side groups by incorporation of phosphine oxide, phosphonate, phosphinate, phosphoric acid, polyphosphate and phosphorylated derivatives [5,15–18], 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 [19–22]. Moreover, it was also reported that some inorganic phosphate-based and zinc-based compounds such as melamine pyrophosphate and zinc hydroxystannate were not only effective flame retardants for the epoxy systems but also could generate a smoke suppressant effect for the resulting thermosets [23,24]. It has been found that the phosphorus-containing moieties form condensed char layer, and the nitrogen-containing ones can release inert nitrogen, ammonia and nitrogen oxide gases to dilute oxygen and facilitate the expansion of the layers during the combustion of the resulting epoxy thermosets [21]. 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 [15,19]. However, these phosphorus- and nitrogen-containing epoxy thermosets hardly gain high weight fractions of phosphorus and nitrogen, resulting in a low degree of flame retardancy [25,26]. There is also a challenge involving the achievement in high mechanical and thermal 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 and thermal properties.

Polyphosphazenes are a unique class of hybrid inorganic–organic polymers based on a repeating motif of 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 makes the inherently flammable organic polymers an auto-extinguishability [29,30]. This feature makes polyphosphazenes particularly good candidates as the flame-retardant materials for electric and electronic applications. It is believed that, when polyphosphazenes or phosphazene-based derivatives are incorporated into the network of a thermosetting polymer, the flame-retardant properties of the resulting thermoset can be effectively improved because of the flame-retardant synergistic effect from the phosphorous–nitrogen combination. A numerous studies were carried out to design and synthesize the flame-retardant epoxy polymers with cyclotriphosphazene moieties in the star-like, cycloliner, and spirocyclic structures [31–35]. However, it was found that the resultant epoxy resins hardly achieved the overall flame resistance, because, in most cases, only a few cyclotriphosphazene units as an effective flame-retardant entity could be incorporated into the epoxy macromolecules through the inter-reaction due to their steric effect [36].

Recently, the phosphazene-based polymers with a cyclomatrix network have attracted a great interest, since such a cyclomatrix-type structure not only introduces much more cyclotriphosphazene rings into the polymeric network but also leads to a high crosslinking density [37]. This may impart much better thermal and flame-retardant properties to the resulting polymers. Although some reported investigations indicated that the cyclomatrix polyphosphazenes have more effective flame retardancy than the other phosphazene-based polymers, their further applications in epoxy resins are seldom reported [38]. In this work, we attempted to design and prepared an epoxy thermosetting system based on the phosphazene-cyclomatrix network. The preparation and characterization of this new system were described, and the thermal crosslinking behaviors, thermal stabilities, and flammability characteristics were investigated. It is highlighted that this thermosetting material is free of halogen elements but has excellent flame resistance, and it shows a potential for the application in electronic and microelectronic fields as an environmentally friendly and nonflammable material.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (HCCP) was purchased from Shanghai Yagu Chemical Co. Ltd., China. It was purified by recrystallization from *n*-heptane, followed by vacuum sublimation at 50 °C with a vacuum degree of 0.1 mm Hg prior to use. Ethylenediamine (EDA), dichloromethane (CH₂Cl₂), triethylamine (TEA), ethanol, *n*-hexane, acetone, and 2-methylimidazole (2-MI) were purchased from Beijing Chemical Reagent Co., China. These chemicals and reagents were used as received without further purification. Diglycidyl ether of bisphenol-A (DGEBA) with an epoxy equivalent weight (EEW) of 196 g/equiv. was kindly supplied by Wuxi Resin Factory of BlueStar New Chemical Materials Co. Ltd., China.

2.2. Preparation of epoxy thermosets containing cyclomatrix phosphazene

A phosphazene-based precursor, 1,1,3,3,5,5,-trispiro(ethylene-diamino)-cyclotriphosphazene (TEDCP), was synthesized first by the reaction of HCCP with EDA. In a typical process: a 2000-mL four-necked round-bottom flask equipped with a thermometer, a reflux condenser, a dropping funnel, and a mechanical stirrer was filled with nitrogen atmosphere and then was charged with a solution of HCCP (139 g, 0.4 mol) in CH₂Cl₂ (800 mL). Sequentially, a solution of EDA (160 mL, 2.4 mol) in CH₂Cl₂ (120 mL) was added dropwise into the flask over 3 h with a vigorous agitation, and meanwhile, the reaction mixture was cooled with an ice bath. With a continuous reaction for 72 h at room temperature, the reactant suspension was filtered and then was added into a mixture solvent of TEA and ethanol (800 mL, TEA/ethanol = 1/1 (vol/vol)) with stirring for 24 h at room temperature. The reactant mixture was filtered, washed with hot water, and then dried under vacuum. Finally, a white crystalline solid was obtained as TEDCP (98.9 g, yield 80.1%).

The epoxy thermosetting system based on phosphazene-cyclomatrix network was prepared through the crosslinking reaction of DGEBA with different amounts of TEDCP using 2-MI as a crosslinking accelerator. In a typical crosslinking process: DGEBA (93.5 g, 0.48 mol), TEDCP (23.4 g, 0.08 mol), and 2-MI (0.35 g, 4.3 mmol) were dissolved in 200 mL of acetone. The mixture was stirred continuously for 1 h to achieve a homogeneous and transparent solution, and then the solvent was removed by rotatory evaporation under reduced pressure. The resulting slurry

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