



# Synthesis and characterization of a novel epoxy resin based on cyclotriphosphazene and its thermal degradation and flammability performance



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## ABSTRACT

The cyclotriphosphazene-based epoxy resin hexa-[4-(glycidylloxycarbonyl) phenoxy]cyclotriphosphazene defined as CTP-EP was successfully synthesized from hexachlorocyclotriphosphazene, *p*-hydroxybenzaldehyde and epichlorohydrin. Its chemical structure was characterized by Fourier transform infrared (FTIR) spectroscopy, <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR spectroscopy. The prepared compound was cured with diamino diphenyl methane (DDM), diamino diphenyl sulfone (DDS) and *m*-phenylenediamine (mPDA), respectively. The flame retardant properties, thermal degradation behavior and flame retardant mechanism of the cured CTP-EP were investigated. The LOI values of all cured CTP-EP samples increased from 19.9% for cured diglycidyl ether of bisphenol-A (DGEBA) to above 30% and successfully passed UL-94 V-0 rating, which demonstrated that the prepared CTP-EP thermoset exhibited excellent flame retardancy. The dynamic mechanical thermal analysis (DMA) test demonstrated that the glass transition temperature (*T*<sub>g</sub>) enhanced from 155 °C for the cured DGEBA to 167 °C for CTP-EP thermoset. The results of thermogravimetric analysis/infrared spectrometry (TG-IR) tests suggested that the phosphazene group and high aromatic content in CTP-EP thermoset stimulated the dehydration of the matrix at earlier degradation process and the formation of char layer, which retarded the release of pyrolysis gas and enhanced the thermal stability of the cured CTP-EP at high temperature. The cone calorimeter tests (cone) test revealed that heat release rate (HRR), total heat release (THR), smoke production rate (SPR) and total heat production (TSP) of the cured CTP-EP decreased significantly compared with the cured DGEBA. The scanning electron microscopy (SEM) results showed that the phosphazene groups in CTP-EP obviously stimulated the formation of the intumescent, compact and stable char layer, which enhanced the flame retardancy of the matrix during combustion. Consequently, the underlying materials were protected from further degradation and combustion during a fire and result in the efficient flame retardancy of CTP-EP thermoset.

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## 1. Introduction

Epoxy resins are important thermosetting materials and have been widely used as advanced composite matrices in various areas from surface coatings, adhesives, automobiles to space vehicles, shipping and electronic/electrical industries for their outstanding properties, such as good mechanical properties, chemical resistance, excellent electric insulating property and low manufacturing cost [1–3]. However, the flammability of epoxy resins leads to fire

disaster inevitably, which severely limits their functional applications. Therefore, the epoxy resins are subjected to various mandatory controls for safety reasons [4,5].

Traditionally, brominated reactive compounds are used as comonomers with epoxy resins to obtain fire-retarded materials. However, flame-retarded 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 [6–8]. Recently, in consideration of environmental problems, researches for halogen-free flame retardant epoxy resins have attracted a great deal of attentions. Organophosphorus molecules are efficient radical scavengers and flame quenching materials. Combustion processes

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are essentially exothermic free radical reactions, so the existence of radical stabilizers impedes combustion by the quenching mechanism. On the other hand, the nitrogen-containing compounds can release the inert gaseous by-products to form a highly porous char that provides thermal insulation and prevents the combustion from spreading [9–12]. There are lots of works reported about the molecular design and synthesis of flame retardant epoxy resins as well as a reactive flame-retardant additives by incorporating phosphorus-containing flame retarding units such as phosphine oxide, phosphates, and other phosphorylated and phosphonylated derivatives [13–19]. Today [18,19] developed a series of phosphorus-containing amines (TEDAP, TMPDAP and TOPDAP) which acted as flame retardant crosslinking agents in epoxy resins. The tests results showed that the epoxy resins with more than 2 wt % phosphorus content could reach excellent flame retardancy. However, these phosphorus-containing epoxy resins have some disadvantages, such as poor resistance to acid and base, low weight fraction of phosphorus, which is resulting in a low degree of flame retardancy [20,21]. Currently, a great interest is focusing on the design of both the backbone and the side groups of epoxy resins with more highly flame retarding moieties like phosphazenes, particularly cyclotriphosphazenes [22–26]. Many researchers have reported the phosphazene-based family of materials because they not only possess a wide range of thermal and chemical stabilities, but also can improve the thermal and flame retardant properties to polymers and their composites [27–34]. El Gouri M [27,28], synthesized a novel epoxy resin (HGCP) which was used as a reactive flame retardant and then blended with pure DGEBA to prepare flame retardant epoxy resins. The results showed that the addition of HGCP could effectively improve the thermal stability of DGEBA and exhibited self-extinguishing characteristics. Wang XD [29] synthesized a novel cyclotriphosphazene-based epoxy compound (PN-EPC) as a halogen-free reactive flame retardant. The tests revealed that the incorporation of PN-EPC could impart excellent flame retardancy to the epoxy thermoset, increased the glass transition temperature and thermal stability of the thermoset and the cyclotriphosphazene rings acted in both condensed and gaseous phases. Hexachlorocyclotriphosphazene is a versatile starting oligomer for the synthesis of phosphazene-based polymers because there are two chlorine groups attaching to each phosphorus atom in cyclotriphosphazenes which are active to be substituted by different nucleophiles. Multiple functions can be realized by replacing the chlorine groups with various functional substituents [35–39]. Once the cyclotriphosphazene is incorporated into the network of thermoset polymers, they exhibit unusual properties such as flame retardancy and self-extinguishing ability due to phosphorous and nitrogen flame retardant synergistic effect. The phosphazene-based polymers present more effective flame retardancy than other flame-retardants, which make them a new research focus [40–43]. Previous reports [30,40,42] show that epoxy thermoset containing cyclotriphosphazene units exhibit a potential application in the modern electric industry for their superior flame retardancy and thermal stability. So it is desirable to obtain novel cyclotriphosphazene-based epoxy materials with excellent comprehensive performance. However, the phosphazene used as primary component for synthesizing the flame retardant epoxy resins was seldom reported [24,27,29,30] and the flame retardant mechanism needs to be further investigated.

In this work, the cyclotriphosphazene-based flame retardant epoxy resin hexa-[4-(glycidylloxycarbonyl)phenoxy] cyclotriphosphazene (CTP-EP) was synthesized. Its chemical structure was characterized by FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR. The thermal stability, flame retardancy, thermal decomposition behaviors and flame retardant mechanism of the synthesized CTP-EP thermoset were investigated by limiting oxygen index (LOI),

vertical burning test (UL-94), thermogravimetric analysis (TGA), thermogravimetric analysis/infrared spectrometry (TG-IR), cone calorimeter tests (cone) and scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Materials

Hexachlorocyclotriphosphazene (HCCP) and 4-hydroxybenzaldehyde were purchased from Wuhan Yuancheng Chemical Co. Ltd., China. Tetrahydrofuran (THF), triethylamine (TEA), ethyl acetate (EA), sodium hydroxide (NaOH), potassium permanganate ( $\text{KMnO}_4$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd., China. Diamino diphenyl methane (DDM), diamino diphenyl sulfone (DDS), m-phenylenediamine (mPDA), epichlorohydrin (ECH) and benzyltriethylammonium chloride (TEBA) were purchased from Aladdin reagent (Shanghai) Co. Ltd., China. Diglycidyl ether of bisphenol-A (DGEBA) (E-44, epoxide equivalent weights = 213 g/epoxide) of technical grade was supplied by Guangzhou Fude Chemicals Industry Co. Ltd., China.

### 2.2. Synthesis of CTP-EP

The final compound, hexa-[4-(glycidylloxycarbonyl)phenoxy] cyclotriphosphazene (CTP-EP), was prepared according to the following three steps and the synthesis routes are shown in Scheme 1.

#### 2.2.1. Synthesis of hexa-(4-aldehyde-phenoxy)-cyclotriphosphazene (HAPCP)

35 g (0.28 mol) 4-hydroxybenzaldehyde dissolved in 150 mL THF and 28 g (0.28 mol) triethylamine as the acid scavenger agent was added into a four-necked-flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet. 14 g (0.04 mol) hexachlorocyclotriphosphazene (HCCP) dissolved in 50 mL THF was added dropwise into the flask continuously and slowly under nitrogen atmosphere at room temperature. The reaction mixture was heated slowly to the reflux temperature and then allowed to stir strongly for 24 h. After that, the mixture was filtered twice to remove triethylamine hydrochloride. The solution was concentrated on a rotary evaporator and then poured into a large amount of water to precipitate the crude product. The compound HAPCP was recrystallized and purified by ethyl acetates following the procedure according to the reported literature [37] and the yield was 31.6 g (92%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 9.9(6H, -CHO) and 7.13–7.75 ppm (24H,  $-\text{C}_6\text{H}_4$ ).

#### 2.2.2. Synthesis of hexa-(4-carboxyl-phenoxy)-cyclotriphosphazene (HCPCP)

According to our previous work [36], hexa-(4-carboxyl-phenoxy)-cyclotriphosphazene (HCPCP) was obtained from oxidizing hexa-(4-aldehyde-phenoxy)-cyclotriphosphazene (HAPCP) by potassium permanganate. 33.3 g potassium permanganate (0.21 mol), 6.3 g sodium hydroxide (0.16 mol) and 320 mL  $\text{H}_2\text{O}$  was added to the solution of 21 g HAPCP (0.024 mol) in 400 mL THF in a three-neck-flask equipped with a mechanical stirrer and refluxing condenser, then the reaction mixture was stirred for 30 h at refluxing temperature. After removing THF in the mixture on a rotary evaporator, the crude product deposited from adding sulfuric acid. The white precipitate was collected by filtration and washed with a great deal of water, then dried in vacuum at 60 °C and the yield was 22.7 g (97%).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  = 12.95 (6H, -COOH) and 7.85, 6.90(24H,  $-\text{C}_6\text{H}_4$ ).

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