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Synthesis of N-P-Si synergistic flame retardant and its effect on the properties of epoxy resin

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Abstract*：A novel P-N-Sisynergistic flame retardant,hexa((2-ethoxy-3-(γ-Trimethoxysilyl) propoxy) propoxy) cyclotriphosphazene (HPCP)was synthesized. The effect of reaction time,mole ratio of reactant and reaction temperature on the product yield was discussed.The structure of HPCP was confirmed by FT-IR and ^{1}H NMR. HPCP was added into epoxy resin (E-51) to prepare flame-retardant modified composites (E-HPCP). The thermal stability (TG) and limiting oxygen index (LOI) of E-HPCP were measured, and the surface morphology of carbon residue after combustion of E-HPCP was analyzed by SEM. The results showed that the yield of HPCP could reach 62.19% when n(KH560):n(HCCP)=7:1, and the reaction time was 120 min at 70°C. The LOI of E-HPCPcan reach 27.1%, which is 35% higher than that of E-51 without flame retardant. A dense carbon layer was formed after combustion, which indicated that HPCP had a good flame retardant effect on E-51.*

***Key words*：** *Hexachlorocyclotriphosphazene; KH560; Synergy; Flame retardant*

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I. Introduction

Flame retardants play an important role in fire prevention and disaster reduction and protecting people's lives and property. At present, the flame retardancy of materials is mainly improved from the following four aspects: adding small molecule flame retardant; Incorporation of flame retardant polymers; Introducing side chains or groups with flame retardant function on the main polymer chain, such as groups containing N, P and halogen; Flame retardant functional structural units[1-4] are introduced into the main polymer chain;. Among them, additive flame retardants have always occupied an absolute share in the flame retardant market due to their advantages of convenient use, low cost and no obvious impact on the properties of main materials [5-9].

Cyclotriphosphazene and its derivatives have been widely used as flame retardant additives for various materials because of their special structure and flame retardant properties. In particular, Si containing derivatives of cyclotriphosphazene, which combine many characteristics of three flame retardant elements P, N and Si, have good synergistic effect, and have been called research hotspots[10-12]. Zhang prepared a P-N-Si synergistic flame retardant material by reacting p-nitrophenol phosphorus chloride with layered bimetallic hydroxide containing Si-Ni-Mg-Al which is used for flame retardant of polyurethane. When 8% of the above flame retardant is added into, it can show good flame retardant performance[13]; Qu designed four flame retardant systems with cyclotriphosphazene, SiO_2, polyhedral oligomeric silsesquioxane (POSS) and graphene by microcapsule flame retardant technology and used them to flame retardant epoxy resin (EP). The maximum limit oxygen index (LOI) value reached 30.5%, and UL-94 test was V-1, which improved the flame retardant performance [14].

In this article, hexa((2-ethoxy-3-(γ-Trimethoxysilyl) propoxy) propoxy) cyclotriphosphazene (HPCP) was synthesized from hexachlorocyclotriphosphazene (HCCP), γ-Glycidyl ether oxypropyl trimethoxysilane (KH560).HPCP has good structural symmetry, stable chemical properties and good compatibility with polymer substrate. The flame retardant spline (E-HPCP) was obtained by adding HPCP into epoxy resin (E-51). The effect of HPCP on the flame retardant properties of E-51 was discussed.

II. Experimental

Hexachlorocyclotriphosphazene (HCCP, 98%) and E-51 used in this study was obtained from Aladdin Reagent Co., Ltd; KH560 was obtained fromMarkun Reagent Co., Ltd; Tetrahydrofuran (THF, A.R.), triethylamine and absolute ethanol was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd.

Under the protection of N_2, KH560 was added into a 250 ml three mouth flask equipped with a dropping funnel, thermometer and spherical condenser tube. 10ml absolute ethanol was dropped in via the dropping funnel for 20minutes when heated to 50°C, then 5 drops of HCl was added into, reflux for 60 minutes and cool to 20°C to obtain KH560-EtOH.KH560-EtOH was dropped into three mouth flask with 6.95 g (0.02 mol) HCCP, 80 ml THF and a certain amount of triethylamine via the dropping funnel for 20 minutes, heating and stirring, and continue to reflux for a period of time after dropping for 30 min. Transfer to the rotary evaporator to evaporate THF, filter by suction, wash with distilled water twice, and dry the filter cake for 120 minutes to obtain dry HPCP. The synthetic route of HPCP is shown in Figure 1.

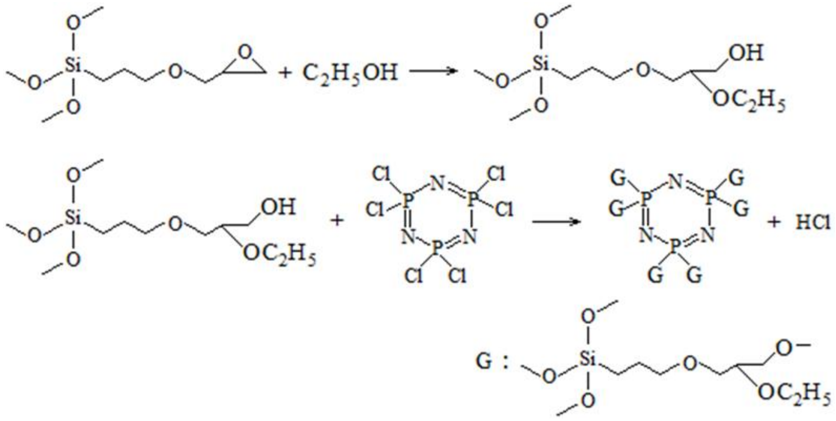


Figure 1. Synthetic route of HPCP

Triethylenetetramine (TT) is selected as the curing agent. After mixing E-51 and TT according to the mass ratio m(E51): m(DT) = 100∶12.4,HPCP passing through a 100 mesh sieve was added according to a certain proportion. They were mixed, defoaming and transferred to the flame retardant spline mold. It is pre-cured at room temperature for 5-10 minutes, and then cured at 60 °C for 30 minutes. After taking out the demoulding, epoxy resin flame retardant spline (E-HPCP) were obtained. Contents of E-HPCP are shown in Table 1.

Table 1 Content of flame retardant epoxy resin spline (E-HPCP)

No.	E-51 /g	TT /g	HPCP /phr
a	100	12.4	0
b	100	12.4	10
c	100	12.4	20
d	100	12.4	30
e	100	12.4	40

III. Results And Discussion

Effect of material ratio on yield of HPCP

HPCP was prepared by refluxing the reactant KH560-EtOH and HCCP at 70 °C for 120 min with THF as solvent at differentratio of HCCP to KH560 (defined as *r*). Since KH560 and excess ethanol are prone to ring opening addition reaction under the catalysis of HCl to generate intermediate KH560-EtOH, the effects of different *r* on the yield (defined as*P*) of HPCP are shown in Table 2 without considering the effect of KH560-EtOH yield.

Table 2 Effects of different r on the yield P of HPCP

r	5.5	6	6.5	7	7.5
P /%	51.74	52.86	54.17	62.19	51.81

It can be seen from Fig.1 that the stoichiometric ratio of HCCP to KH560is r = 6:1. It can be seen from table 2 that when r<7, the product yield shows an upward trend; When r=7, the yield was the highest; When r>7, the yield decreased. Although excess KH560 could improve the conversion of HCCP, it also caused side reactions, which reduced the yield of the target product. In conclusion, when n(KH560): n(HCCP) =7∶1, the highest yield of HPCP was 62.19%.

Effect of reaction temperature on yield of HPCP

HPCP was prepared by using THF as solvent, r=7, refluxing at different temperatures (defined as$T$/°C) for 120 min. The effects of different T on the yield of HPCP are shown in Table 3.

Table 3 Effects of different T on the yield of HPCP

T	65	70	75	80
P /%	58.9	62.19	55.82	52.53

It can be seen from table 3 that when *T*<70°C, the product yield shows an upward trend; when *T*>70 °C, the yield decreased, and when *T*=70°C, the yield was the highest. When the reaction temperature is low, the molecular thermal movement speed is slow, resulting in slow reaction speed, and some reactants may be wrapped by the product, resulting in low yield. On the contrary, KH560 is prone to cross-linking, resulting in abnormal reaction and affecting the yield. In conclusion, when the reaction temperature was 70°C, the highest yield of HPCP was 62.19%.

Effect of stress time on yield of HPCP

HPCP was prepared by using THF as solvent, *r*=7, and refluxing at 70°C for different reaction time (defined as *t*/minutes). The effects of different *t* on the yield of HPCP are shown in Table 4.

Table 4 Effects of different t on the yield of HPCP

t/minutes	60	90	120	150
P /%	36.99	40.47	62.19	51.43

It can be seen from table 4 that when *t*<120 minutes, the product yield shows an upward trend; when *t*>60 minutes, the yield decreased, and when *t*=60 minutes, the yield was the highest. Due to the special ring structure of HCCP, the Cl atom in the molecule is easy to react with the active H atom on -OH in the intermediate KH560-EtOH. Therefore, compared with other organic synthesis, this reaction speed is faster. When the reaction was less than 120 minutes, the reaction could not be carried out completely and the yield was low; when the reaction is longer than 120 minutes, although sufficient time is provided for the full reaction of the material, some by-products may be produced. In conclusion, when the reaction time was 120 minutes, the highest yield of HPCP was 62.19%.

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectroscopic measurements of KH560 and HPCP were recorded on aNicolet IS 10 FT-IR spectrophotometer at 25°C, wherein 32 scans with a spectral resolution 1cm^{-1} were collected during each spectroscopic measurement.Figure 2 illustratestypical FTIR spectra of KH560 and HPCP.

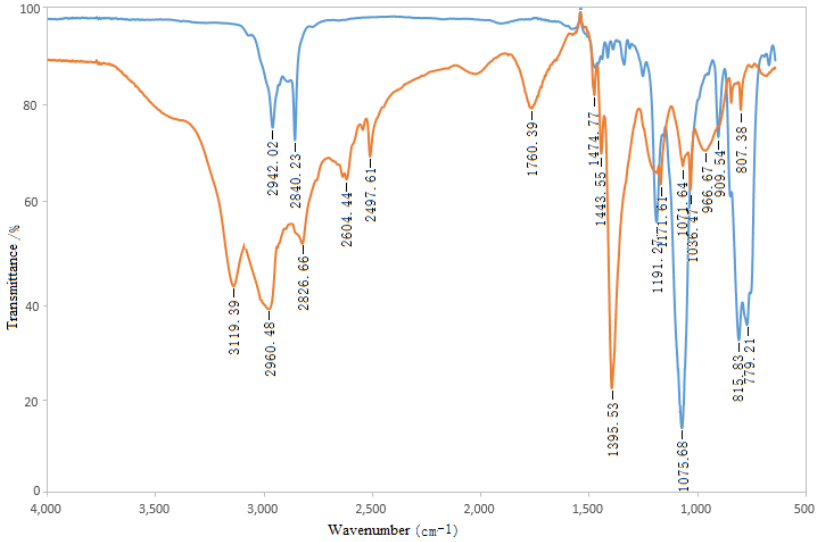


Figure 2.FT-IR spectra ofKH560 and HPCP

It can be seen from Fig. 2 that the absorption peak of 1036 cm^{-1}should be attributed to the resonance absorption of P-O-C bond. The positions of the above other absorption peaks are consistent with those reported in literature [15-16]. In conclusion, because P-O-C bond is generated, it can be preliminarily determined that the product is HPCP.

Nuclear magnetic resonance hydrogen spectrum analysis (^{1}H NMR)

^{1}H NMR spectroscopic measurements of HPCPwere recorded on aMicroMR12-025V. Figure 3 illustrates^{1}H NMR spectra of HPCP.

It can be seen from Fig.3 that the compound has H atoms in 9 chemical environments. The absorption peak at 3.49and 2.59 ppm should be attributed to the hydrogen atom in ethoxy group(i.e. a and b in the structural formula),respectively; the absorption peak at 3.73, 3.14 and 2.78 ppm should be attributed to the hydrogen atom on -CH_2- connected to the O atom (i.e. c, e and f in the formula), respectively; the absorption peak at 3.58 ppm should be attributed to the hydrogen atom on -OCH_3 (i.e. i in the formula); the absorption peak at 3.38 ppm should be attributed to the tertiary hydrogen atom on C connected to ethoxy group (i.e. d in the formula); the absorption peak at 1.71 ppm should be attributed to the hydrogen atom on -CH_2- (i.e. g in the formula); the absorption peak with a chemical shift of 0.67 ppm is the hydrogen atom on -CH_2- connected to Si (i.e. h in the formula) [17].

Combined with the infrared spectrum data in the previous section, it can be confirmed that HPCPwas successfully prepared.

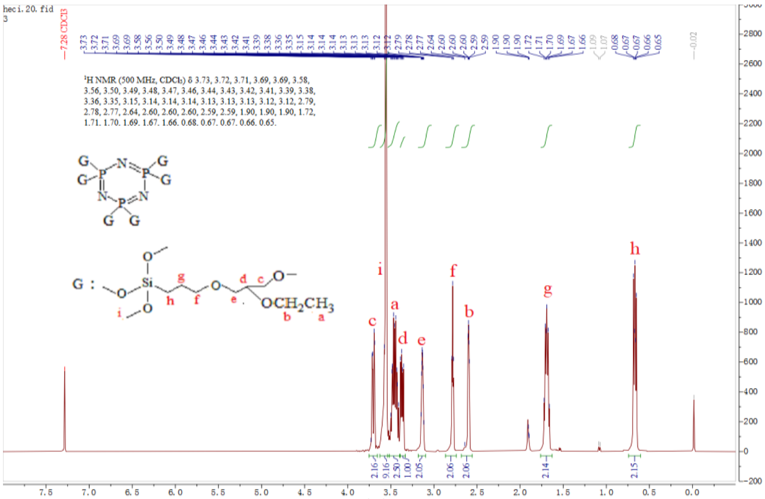


Figure 3.^{1}H NMR spectra of HPCP

Thermogravimetric analysis (TG)

Dta7300 thermogravimetric analyzer was used to analyze the thermal stability of E-HPCP. The TG of epoxy resin flame retardant splines with HPCP contents of 0 phr, 10 phr, 20 phr, 30 phr and 40 phr are shown in Fig. 4. The initial decomposition temperature and mass fraction of residual carbon after combustion are listed in Table 5 respectively.

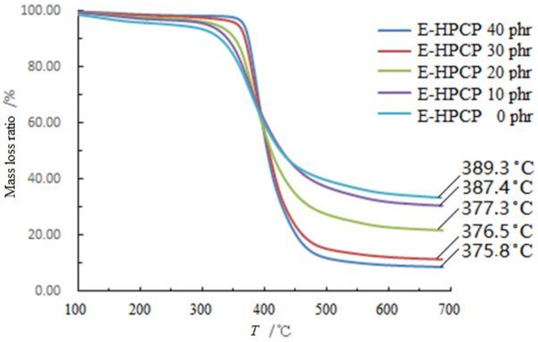


Figure 4.TG of E-HPCP samples

According to Fig. 4, the decomposition temperature (T_{max}) of pure epoxy resinis 389.3°C. With the increase of HPCP content, T_{max} of E-HPCP series samples decreased gradually from 389.3 to 375.8°C. This shows that the added HPCP flame retardant makes the epoxy resin matrix decompose in advance[13].

It can be seen from table 5 that the initial decomposition temperature of pure epoxy resin spline is 366.67 °C. With the increase of HPCP content in epoxy resin, the initial decomposition temperature of E-HPCP gradually decreased. When the HPCP content increased from 10 phr to 40 phr, the initial decomposition temperature of E-HPCP decreased from 357.48°C to 256.75°C, down by about 100°C. The mass fraction of residual carbon of pure epoxy resin is 9.29% at 600°C and 8.64% at 700°C; when the content of HPCP increased from 10 phr to 40 phr, the mass fraction of residual carbon increased from 12.18% to 34.80% at 600°C and from 11.39% to 33.40% at 700°C. It shows that HPCP can effectively form a carbon system with epoxy resin and work together to improve the yield of residual carbon, which helps to reduce the amount of gas-phase combustibles decomposed by epoxy resin and reduce the heat release of combustion**[12]**. Moreover, the carbon layer has a beneficial effect on isolating O_2 and heat in the combustion area from entering the interior of the material. At the same time, it can well control the escape of combustible gas and protect the degradation of internal materials[11].

Determination of oxygen index (LOI)

The limiting oxygen consumption index LOI measurements of E-HPCPwere tested on aJF-3 oxygen indextester.LOI test is conducted for E-HPCP with HPCP content of 0 phr, 10 phr, 20 phr, 30 phr and 40 phr respectively according to GB/T 2406.2-2009. The combustion performance is listed in Table 5.

Table 5 Combustion performance of E-HPCP

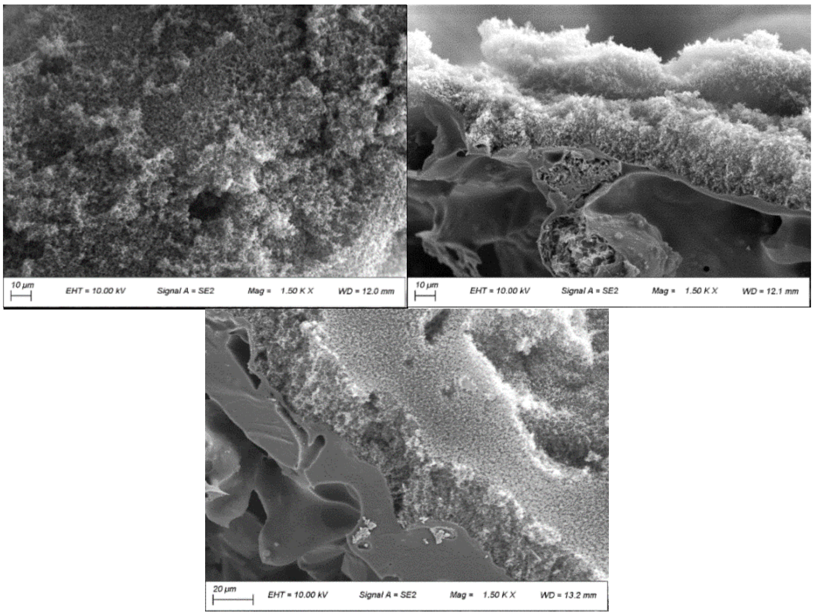
content of HPCP/phr	LOI/%	$T_{5\%}$ /°C	$T_{\max}$ /°C	mass fraction of residual carbonat 600°C/%	mass fraction of residual carbonat 700°C /%
0	19.8	366.67	389.3	9.29	8.64
10	23.6	357.48	387.4	12.18	11.39
20	24.5	323.43	377.3	22.83	21.76
30	25.5	309.66	376.5	31.83	30.54
40	26.9	256.75	375.8	34.80	33.40

Note: The temperature when the weight loss is 5% is called the initial decomposition temperature, which is recorded as$T_{5\%}$.

It can be seen from table 5 that the LOI of pure epoxy resin is 19.8%. Although there is droplet phenomenon, it is not enough to ignite absorbent cotton. With the increase of HPCP content, the oxygen index of E-HPCP increased gradually. When the content of HPCP increased from 10 phr to 40 phr, the LOI of E-HPCP increased from 23.6% to 26.9%. This shows that with the continuous increase of HPCP content, the LOI value of E-HPCP also increases, reflecting better and better flame retardant performance.

Surface morphology analysis of residual carbon (SEM)

The surface morphology of residual carbon after combustion was analyzed by Sigma 500 electron scanning microscope underthe test voltage was 10 kV.The surface morphology of residual carbon after E-HPCP combustion with HPCP contents of 0 phr, 20 phr, and 40 phr is shown in Fig. 5, respectively.



(a)pure E-51 (b)E-HPCP-20 phr(c)E-HPCP-40 phr

Figure 5.The surface morphology of residual carbon after E-HPCP combustion

As can observed in Fig. 5(a), a relatively uniform carbon layer is obtained after pure E-51 spline combustion. However, the residual carbon is not dense enough and there are many holes, which mean that most combustible gases can pass through the holes and reach the surface of the object during the combustion process, so as to make the combustion more intense. At the same time, the heat can be rapidly released to the interior of the object and make the matrix decompose rapidly[18].

It can be seen from Fig. 5(b-c) that with the increase of HPCP content, the residual carbon after combustion becomes denser and the amount of residual carbon becomes larger and larger (consistent with TG data, the mass fraction of residual carbon increases from 12.18% to 34.80% at 600°C and 11.39% to 33.40% at 700°C), the carbon layer becomes thicker and thicker, and there are no obvious holes. The carbon layer can effectively isolate the release of combustible gas and heat transfer in the combustion process, which not only delays the combustion fundamentally, but also protects the base material.

IV. Conclusion

A novel P-N-Sisynergistic flame retardant, hexa ((2-ethoxy-3-(γ-Trimethoxysilyl) propoxy) propoxy) cyclotriphosphazene(HPCP) was synthesized. The optimum preparation conditions of HPCP were discussed, and the structure of the target product was confirmed by FT-IR and ^{1}H NMR.When the material ratio *n*(KH560):*n*(HCCP)=7:1 and the reaction time was 120 minutes at 70°C, the highest yield of HPCP was 62.19%. When the amount of HPCP was 40 phr, the thermal stability of the epoxy flame retardant spline was excellent, and the LOI was 26.9%, which was 35% higher than that of E-51 without flame retardant. A dense carbon layer was formed after combustion, indicating that HPCP had a good flame retardant effect on E-51.

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