

Synthesis of a Polyhedral Oligomeric Silsesquioxane (POSS) containing Phenyl and DOPO (7Ph-T7-DOPO) and its thermal stability

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Abstract. A new type of polyhedral oligomeric silsesquioxane (POSS) (7Ph-T7-Vinyl) containing phenyl and 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was synthesized from phenyltrimethoxysilane, trichlorovinylsilane, and DOPO in high yield. This product was subjected to addition reaction using an AIBN catalyst in toluene. The structure of 7Ph-T7-DOPO was characterized by ¹HNMR and FTIR, and 7Ph-T7-DOPO exhibited a crystal structure of (RSiO_{1.5})_n. TGA curve analysis showed the high thermal stability of the cage-like compound. The flame-retardant properties of the EP composites were also tested in terms of limiting oxygen index (LOI) and UL-94. Incorporation of 2.5 wt. % DOPO-POSS into epoxy resin (EP-2.5) resulted in an LOI of 27.5 and UL-94 rating of V-1 (t₁ = 34 s and t₂ = 0 s). All of these results suggested that the 7Ph-T7-DOPO exhibited high thermal stability.

1. Introduction

Organic-inorganic hybrid composites combine the advantages of inorganic materials and organic polymers. Such composites are generally considered to be a new generation of high-performance materials. Polyhedral oligomeric silsesquioxanes (POSS) are cage-like hybrid molecules consisting of silicon and oxygen [1,2]. These compounds can be represented as (RSiO_{1.5})_n, where n is an even number (n ≥ 6), R is hydrogen or any alkyl, alkylene, aryl, arylene, or organofunctional derivative of alkyl, alkylene, arylene groups, and Si-O is the inorganic key [3,4]. Considering that the side group R can result in a diverse array of silsesquioxanes [5], organic-inorganic hybrid materials can facilitate development of high-performance materials that combine the desirable properties of conventional organic and inorganic components; such properties include thermal stability, solubility, and processability [6].

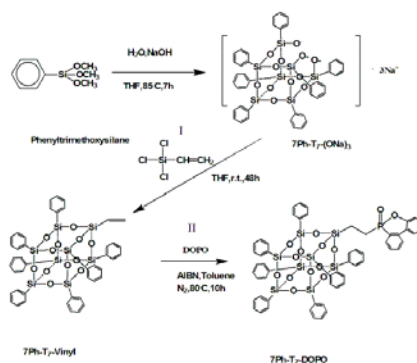


Fig1. Illustration for the synthesis of 7Ph-T7-Vinyl and 7Ph-T7-DOPO

Phosphorus compounds have been investigated in epoxy resins, and findings show that these compounds can impart flame retardancy through flame inhibition in the gas and condensed phases.

DOPO, a cyclic phosphate with a diphenyl structure, exhibits high thermal stability, oxidation resistance, and good water resistance [7]. DOPO is always incorporated into epoxy resins or other polymers to improve their flame-retardant properties and thermal stability [8]. It is believed that the chemical structure of such materials containing both of phosphorus and DOPO would show excellent flame-retard performance. Thus, our project aims to synthesize a new type of caged phosphorus-containing silsesquioxane by introducing DOPO to silsesquioxane molecules.

In this study, we prepared DOPO-POSS via hydrolysis of trichlorosilanes [9] and POSS-containing nanocomposites using simple organic reactions (nucleophilic substitution and radical addition) to introduce different phosphorus substituents to the periphery of silsesquioxanes [10]. A new phosphorus-containing POSS (7Ph-T₇-DOPO) was synthesized via a three-step pathway (Scheme 1), and the structure of the product was characterized by ¹H NMR and FTIR. Thermogravimetric analysis (TGA) and DTG were performed to systematically evaluate the chemical and physical properties of 7Ph-T₇-DOPO, and its EP composites were tested in terms of limiting oxygen index (LOI) and UL-94.

2. Experimental

2.1 Sample preparation

Synthesis of 7Ph-T₇-(ONa)₃. Phenyltrimethoxysilane (91.20 g, 0.46 mol), THF (500 mL), distilled water (10.5 g, 0.58 mol), and sodium hydroxide (7.9 g, 0.2 mol) were charged into a three-necked flask equipped with a reflux condenser. The mixture was refluxed at 85 °C for 7 h with magnetic stirring. The system was cooled to room temperature and left for another 6 h. THF was then distilled off until a white solid substance was obtained.

Synthesis of 7Ph-T₇-Vinyl. THF (450 mL) was used to dissolve 7Ph-T₇-(ONa)₃, and trichlorovinylsilane (4 mL) was gradually added dropwise into a three-necked flask by syringe. The mixture was stirred at room temperature for 48 h to obtain a white powder (10.45 g, yield: 44.95%).

Synthesis of 7Ph-T₇-DOPO. 7Ph-T₇-Vinyl (0.88 g, 0.90 mmol), DOPO (0.3687 g, 1.707 mmol), AIBN (0.616 g), and toluene (3.5 mL) were added to a small flask. The mixture was then purged with nitrogen for 10 min and magnetically stirred at 80 °C for 10 h to obtain a white product (0.4337 g, yield: 40.36%).

Preparation of DOPO-POSS/EP composites. To realize pre-reaction between DOPO-POSS and epoxy resin, 7Ph-T₇-DOPO was dispersed in diglycidyl ether of bisphenol A (DGEBA) at 140 °C for 2 h before curing. The DOPO-POSS contents in the EP composites were adjusted to 0.5 wt.%. After the system was cooled to 70 °C, the curing agent (m-PDA) was added. The equivalent weight ratio of DGEBA to m-PDA was 25:3. The mixtures were cured at 80 °C for 2 h and then post-cured at 150 °C for 2 h to obtain the product.

2.2 Measurements

¹H NMR were recorded on a Bruker Avance 400 NMR spectrometer operated in Fourier transform mode. CDCl₃ was used as the solvent, and the solution was measured with tetramethylsilane (TMS) as the internal reference.

FT-IR spectra were recorded on a NICOLET 6700 IR spectrometer. Spectra were collected by 32 scans with a spectral resolution of 4 cm⁻¹.

Thermogravimetric/differential thermal analysis was performed at a heating rate of 10 °C /min under a nitrogen atmosphere and the temperatures ranging from room temperature to 800 °C.

LOI was obtained based on the GB/T2406-93 standard by measuring the minimum oxygen concentration required to support candle-like combustion of EP. An oxygen index instrument (Rheometric Scientific Ltd.) was used on barrels with dimensions of 100 mm × 6.5 mm × 3 mm.

Vertical burning tests were performed based on the UL-94 standard with samples measuring 125 mm × 12.5 mm × 3.2 mm. In this test, the samples were classified as V-0, V-1, V-2, or unclassified according to behavior (dripping of burning material and burning time).

3. Results and discussion

3.1 7Ph-T7-Vinyl.

7Ph-T₇-Vinyl was obtained from a substitution reaction between 7Ph-T₇-(ONa)₃ and trichlorovinylsilane [Scheme 1(I)]. FT-IR (KBr, cm⁻¹): 3000-3080 (phenyl), 1500-1600 (CH₂=CH₂), 1091 (Si-O), 1091 (Si-O-Si). ¹HNMR (CDCl₃, δ, ppm, TMS): 5.993-6.168 (3H, Si-CH=CH₂), 7.145-7.779 (35H, H in phenyl group).

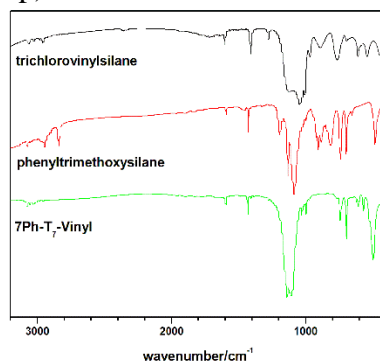


Fig. 1 FT-IR spectra obtained for trichlorovinylsilane, phenyltrimethoxysilane and 7Ph-T₇-Vinyl.

The FT-IR spectra of 7Ph-T₇-Vinyl (Figure 3) indicated the disappearance of the absorbance peak in the region of 2824-2846 cm⁻¹, which is the characteristic of -OCH₃. The characteristics of CH₂=CH₂ at 1500-1600 cm⁻¹ and phenyl at 3000-3080 cm⁻¹ for 7Ph-T₇-Vinyl were attributed to trichlorovinylsilane and phenyltrimethoxysilane, respectively. Characteristic Si-O-Si absorbance at 1091 cm⁻¹ may also be observed.

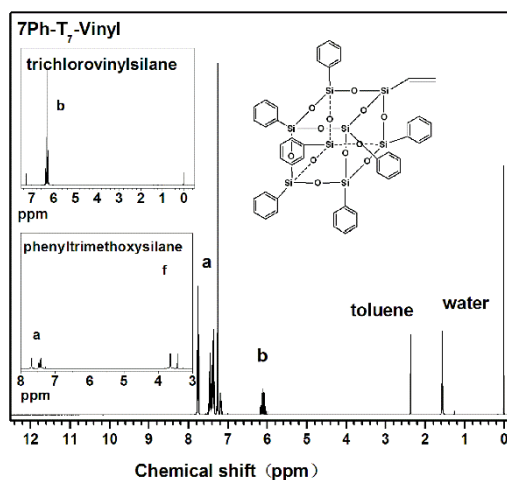


Fig. 2 ¹H NMR spectra obtained for phenyltrimethoxysilane, trichlorovinylsilane and 7Ph-T₇-Vinyl.

The ¹H NMR spectrum showed two signals reflecting the chemical structure of 7Ph-T₇-Vinyl (Figure 2). The peaks at 7.14-7.76 ppm (peak a) and 5.99-6.18 ppm (peak b) are ascribed to phenyl and vinyl groups, respectively. The signal of O-CH₃ at 3.652 ppm (peak f) for phenyltrimethoxysilane also completely disappeared in the spectrum of 7Ph-T₇-Vinyl. The signal at 1.27 ppm may be referenced to toluene, while that observed at 1.5 ppm may be referenced to water.

3.2 7Ph-T7-DOPO.

7Ph-T₇-DOPO was obtained by addition reaction between 7Ph-T₇-Vinyl and DOPO [Scheme 1(II)]; FTIR (KBr, cm⁻¹): 3000-3080 (phenyl and biphenyl), 2890-2940 (CH₂-CH₂), 1477 (P-biphenyl), 1235 (P=O), 1091 (Si-O-Si), 914 (P-O-biphenyl). ¹HNMR (CDCl₃, δ, ppm, TMS): 0.954-1.200 (2H, Si-CH₂-), 2.186-2.263 (2H, P-CH₂-), 7.178-7.940 (43H, H in phenyl and biphenyl).

In the FTIR spectra of DOPO-Vinyl and 7Ph-T₇-DOPO (Figure 3), the characteristic absorbance of CH=CH₂ at 1500-1600 cm⁻¹ completely disappeared compared with that of 7Ph-T₇-DOPO. New peaks at 1235, 1477, 914, and 3037-3100 cm⁻¹ were attributed to P-O, P-biphenyl, P-O-biphenyl, and biphenyl, respectively. Characteristic CH₂-CH₂ absorbance at 2863-2954 cm⁻¹ may also be observed.

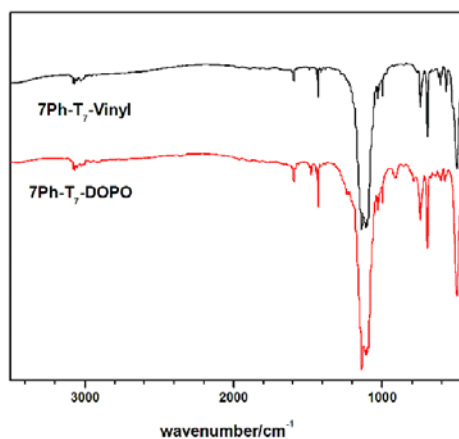


Fig.3 FT-IR spectra of obtained for 7Ph-T7-Vinyl and 7Ph-T7-DOPO.

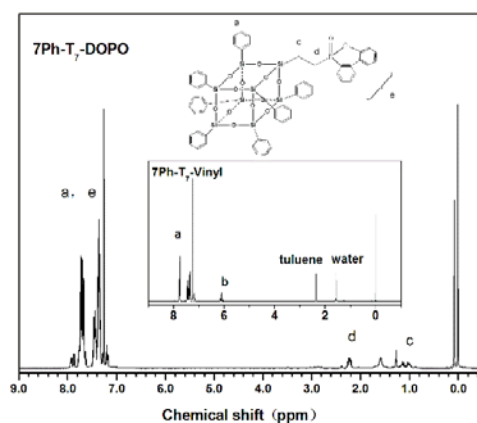


Fig. 4 ^1H NMR spectra of 7Ph-T7-DOPO

Figure 4 shows the ^1H NMR spectra of 7Ph-T₇-Vinyl and 7Ph-T₇-DOPO. The signal at 5.99-6.18 ppm, which is ascribed to the vinyl groups of 7Ph-T₇-Vinyl, disappeared in the spectrum of 7Ph-T₇-DOPO. New signals observed at 2.238, 1.011-1.139, and 127.9-137.59 ppm (peaks c, d, and e) in 7Ph-T₇-DOPO were also ascribed to methylene protons in Si-CH₂, P-CH₂, and biphenyl groups, respectively. The signal at 2.34 ppm was referenced to grease, and that observed at 1.5 ppm was referenced to water.

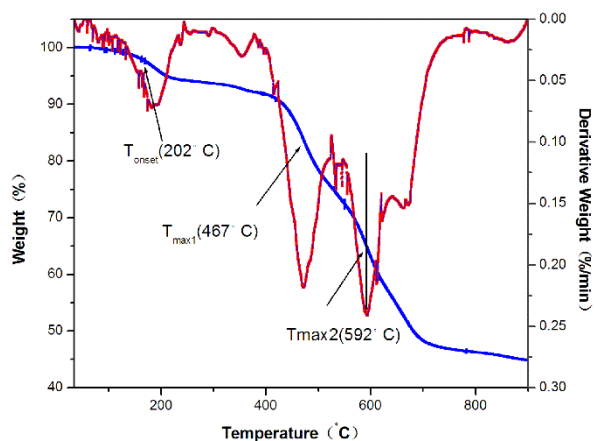


Fig. 5 TGA and DTG curves of 7Ph-T7-DOPO.

3.3 Thermogravimetric analysis of 7Ph-T7-DOPO

The TGA and DTG curves of 7Ph-T₇-DOPO are presented in Figure 6. Four decomposition temperatures (Figure 7) were found: Tonset (202°C), defined as the temperature at which 5% weight loss occurs; Tmax1 (467°C), defined as the temperature at first maximum weight loss rate; Tmax2 (592°C), defined as the temperature at second maximum weight loss rate; and char residue at 850°C. Weight loss in the temperature range of 250-400°C was slow and is attributed to residual silanol in DOPO-POSS. The first rapid weight loss between 400 and 550°C may be ascribed to degradation of DOPO groups. The second rapid weight loss between 550 and 650°C may correspond to phenyl degradation. The remaining residue of 7Ph-T₇-DOPO at 850°C was 46.2%. Thus, 7Ph-T₇-DOPO showed high thermal stability (Figure 6).

3.4 Flame behavior of the cured EP composites

LOI values and vertical burning classifications (UL-94) for EP and 7Ph-T₇-DOPO /EP composites are listed in Table 1.

Incorporation of 2.5 wt. % 7Ph-T₇-DOPO increased the LOI value of epoxy resin from 24.0 to 27.5 compared with that of 0 wt. % 7Ph-T₇-DOPO. Flame retardancy was notably developed in the presence of 7Ph-T₇-DOPO.

UL-94 test results are also shown in Table 1. The epoxy resins with 7Ph-T₇-DOPO clearly gained enhanced flame retardancy. Incorporation of 2.5% 7Ph-T₇-DOPO inhibited dripping and promoted self-extinguishing. The UL-94 rating of resins with 7Ph-T₇-DOPO reached V-2 ($t_1 = 34$ s and $t_2 = 0$ s). All these results indicated that the Polyhedral Oligomeric Silsesquioxane (POSS) containing Phenyl and DOPO (7Ph-T₇-DOPO) synthesized in this work owned excellent thermal stability.

Table 1 Flame retardancy of DOPO-POSS/EP composites.

Samples	Cured epoxy Resin(wt.%)	Content of 7Ph-T ₇ -DOPO (wt.%)	LOI(%)	UL-94 (3.2mm)	t ₁ (s)	t ₂ (s)	Dripping
EP-0	100.0	0.0	24	NR	>30	/	Yes
EP-2.5	97.5	2.5	27.5	V-1	34	0	No

4. Summary

A new type of DOPO-POSS (7Ph-T₇-DOPO) was synthesized by addition reaction between DOPO and 7Ph-T₇-Vinyl. 7Ph-T₇-Vinyl was obtained by a substitution reaction between 7Ph-T₇-(ONa)₃ and trichlorovinylsilane. FTIR and ¹HNMR analyses were used to characterize the structure of the two-cage compound. TGA and DSC tests were also performed to examine the properties of 7Ph-T₇-DOPO. Results indicated that 7Ph-T₇-DOPO exhibited excellent flame-retardant properties. The LOI of 7Ph-T₇-DOPO/EP composites increased from 25 to 27.5, and their UL-94 rating reached V-1.

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