



Improving the fracture toughness and flame retardant properties of epoxy thermosets by phosphaphenanthrene/siloxane cluster-like molecules with multiple reactive groups

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ABSTRACT

To meet the increasingly stringent requirements for the fire safety and mechanical properties of epoxy thermoset (EP) in advanced manufacturing industry, two kinds of phosphaphenanthrene/siloxane cluster-like molecules with multiple reactive groups (TriDSi and TetraDSi) were synthesized, and then linked into the cross-linked network of epoxy thermoset, separately. The incorporated TriDSi and TetraDSi improved the fracture toughness and flame retardant performance of epoxy thermoset, simultaneously. The impact strength of 6%TriDSi/EP and 6%TetraDSi/EP both increased by more than 120%, compared with that of neat epoxy thermoset. Meanwhile, 6%TriDSi/EP and 6%TetraDSi/EP both passed UL94 V-0 rating with a limited oxygen index of 35.2% and 36.0%, respectively. Moreover, the heat release of burning thermoset was also suppressed significantly by incorporated cluster-like molecules. Through segment-aggregation toughening effect and group-aggregation flame retardant effect, the cluster-like molecules TriDSi and TetraDSi endowed epoxy thermoset with superior fracture toughness and significantly lowered combustibility. This study provides a promising choice to manufacture advanced epoxy thermoset materials.

1. Introduction

Advanced material technology is always the foundation and driving force of social development and progress [1–4]. Especially, with the growing concerns on fire safety of organic materials, high-level flame retardant properties have become key indicators for most advanced materials [5–8]. Meanwhile, considering durability and stability, the superior physical and mechanical properties are generally required in advanced materials, too [9–13]. As one of the most common basic raw materials for adhesives [14–16], composites [17–19], and coatings [20–22], epoxy resin has been widely applied in electronic and electrical fields [23–25], in which once there were massive fire hazard occurring frequently, for the heating effect of current and the combustibility of polymer materials. Thus, to meet the increasingly stringent performance requirements, besides satisfactory physical and mechanical properties, the superior flame retardant performance cannot be ignored by most

advanced epoxy thermoset materials, especially [26,27].

To fulfill the superior suppression on combustibility, massive efforts have been made to improve the flame retardant performance of epoxy thermoset by different routes: (1) Intrinsic flame retardant material, introducing specific flame retardant structure into epoxy resin molecule [28–30]; (2) Flame retardant curing agent, constructing curing agent with specific flame retardant structure [31–33]; (3) Flame retardant additive, adding additional additive- or reactive-type flame retardant additive during processing [34–38]; (4) Flame retardant coating, protecting inner pristine bulk material from fire [39]. Thereinto, most researches focused on developing flame retardant curing agents and additives for epoxy resin, especially the structurally diverse additives. In these researches, 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has been frequently utilized to prepare high-efficiency phosphaphenanthrene-containing flame retardant molecules, for its relatively higher chemical reactivity and universal flame retardant

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effectiveness [40–44]. Meanwhile, some works also revealed that, to obtain more sustained and effective barrier and protective effect, the charring effect of only phosphaphenanthrene group needs to be further improved in some aspects [45]. Fortunately, some researches on phosphaphenanthrene-containing bigroup molecules revealed that, it is very likely to achieve more superior flame retardant effect from the group synergistic effect between phosphaphenanthrene group and certain other groups [46–48]. In addition, some former researches reported that, the introduction of siloxane segmer was not only beneficial to enhancing the charring capacity of epoxy thermoset [49], forming higher-quality charring barrier, but also advantageous to toughen thermoset matrix [50], improving the fracture toughness of epoxy thermoset.

Our former research on linear phosphaphenanthrene/siloxane bigroup oligomers (DDSi-n, n means degree of polymerization) revealed that, the flame retardant and toughening performance of bigroup oligomer was influenced not only by phosphaphenanthrene/siloxane specific value, but also by structural construction form of oligomer. The former exposed that the decrease of phosphaphenanthrene/siloxane specific value reduced the flame retardant efficiency of bigroup oligomer, while the latter disclosed that the axial growth of toughening segmer (repeat unit) weakened the toughening effect of bigroup oligomer [51]. Consequently, the flame retardant and toughening performance of phosphaphenanthrene/siloxane bigroup molecule may be further improved by optimizing the following two aspects: (1) Increase phosphaphenanthrene/siloxane specific value in molecule; (2) Use bigroup toughening segmer to construct star-shaped cluster-like molecule. Thereinto, besides the potential toughening benefits, the aggregation of flame retardant groups and toughening segmers in cluster-like molecule perhaps brings extra contributions in inhibiting combustion and improving toughness, for the concentrated release of flame retardant effect and toughening actions from aggregated functional units.

Thus, two kinds of phosphaphenanthrene/siloxane bigroup cluster-like molecules with multiple reactive groups (TriDSi and TetraDSi) were seriatim designed and synthesized, in which the phosphaphenanthrene/siloxane specific value, the phosphaphenanthrene cluster size, and the aggregation level of bigroup toughening segmers in cluster-like molecule all increase gradually, compared with that of the contrastive DiDSi (namely DDSi-1) [51], as shown in Fig. 1. Then, the cluster-like molecules TriDSi and TetraDSi were separately linked into the cross-linked network of epoxy thermoset, as reactive-type additive. The impact strength and combustion behavior of modified epoxy thermoset were detected, to evaluate the indwelling structure-performance relationship. The fracture surface of modified epoxy thermoset was observed, to disclose how TriDSi and TetraDSi induced thermoset matrix to experience ductile fracture. The charring behavior, decomposition process and corresponding volatile thermal decomposition products of modified epoxy thermoset were analyzed, to reveal how TriDSi and TetraDSi

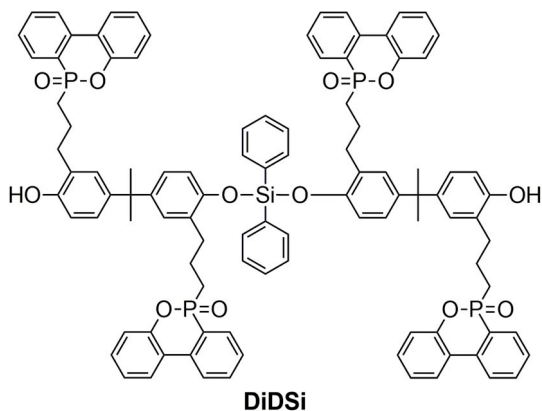


Fig. 1. Chemical structure of the contrastive DiDSi.

suppressed the combustion process of epoxy thermoset. Furthermore, the presumptive pyrolysis routes of TriDSi and TetraDSi were also inferred by identifying their pyrolysis fragments, to cognize what positive fragments were released to inhibit the combustion reaction of epoxy thermoset. Finally, the toughening and flame retardant mechanisms of TriDSi and TetraDSi were concluded, to expound how TriDSi and TetraDSi endowed epoxy thermoset with superior comprehensive flame retardancy and fracture toughness.

2. Experimental

2.1. Materials

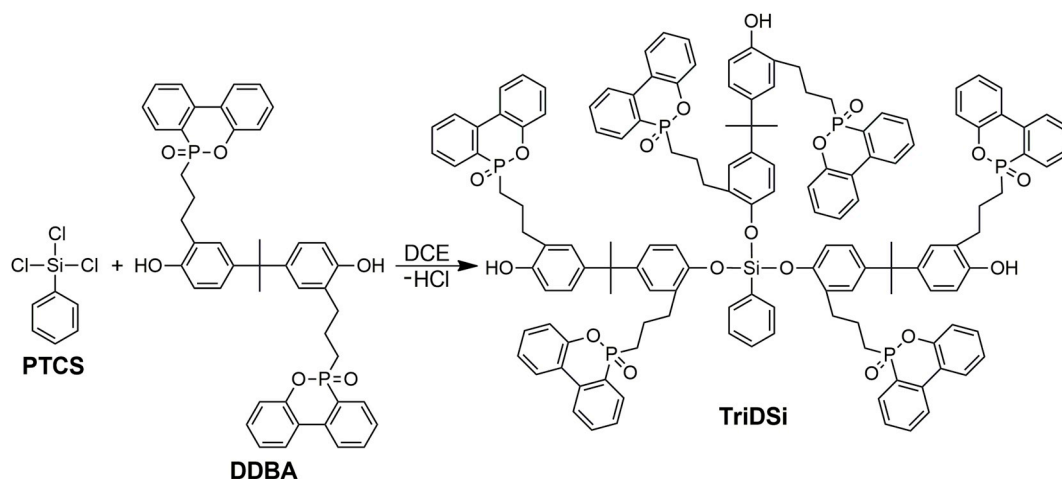
Phenyltrichlorosilane, 1, 2-dichloroethane, 4, 4'-diamino-diphenyl methane (DDM), and benzyltriphenylphosphonium chloride were purchased from J&K Scientific Ltd. (China). Tetrachlorosilane was supplied by Tokyo Chemical Industry Co., Ltd (Japan). DDBA and DiDSi (also called as DDSi-1) were synthesized in our lab [51]. Bisphenol A diglycidyl ether (DGEBA, commercial name: E-51) was acquired from Nantong Xingchen Synthetic Material Co., Ltd. (China).

2.2. Synthesis of cluster-like molecule TriDSi

To dry 1, 2-dichloroethane as much as possible, avoiding phenyltrichlorosilane hydrolysis, the solvent (400 mL) was pre-distilled out 50 mL fraction by vacuum distillation under 100 °C. After that, DDBA (44.45 g, 0.060 mol) was firstly dissolved in pre-dehydrate 1, 2-dichloroethane with mechanical agitation at 85 °C. Then, phenyltrichlorosilane (4.45 g, 0.021 mol) was uniformly added into flask from rubber seal in 5–10 min, using injection syringe. The condensation reaction between DDBA and phenyltrichlorosilane was proceeded at 90 °C for 20 h. The by-product hydrogen chloride was eliminated from condenser pipe, which was successively equipped with drying tube and absorption apparatus. After reaction finished, the solvent and residual hydrogen chloride were preliminarily removed via vacuum distillation at 100 °C. And then, the crude product was put in 180 °C vacuum oven to fully remove residual solvent and hydrogen chloride, forming brittle slight-yellow transparent solid. The reaction formula of TriDSi was shown in Scheme 1. Yield: above 98%. Fourier transform infrared spectrum (FTIR, cm^{-1} , shown in Fig. S1): 3383 and 3231 ($\text{C}_{\text{Ar}}-\text{OH}$); 3063 ($\text{C}_{\text{Ar}}-\text{H}$); 2963 and 2870 (CH_3); 2932 (CH_2); 1607, 1595, 1583, 1561, and 1497 (aromatic skeleton); 1431 ($\text{P}-\text{C}$); 1206 ($\text{P}=\text{O}$); 969 ($\text{Si}-\text{O}-\text{C}$); 914 ($\text{P}-\text{O}-\text{C}$); 755 (o-disubstituted benzene in phosphaphenanthrene). ^1H nuclear magnetic resonance (^1H NMR, ppm, shown in Fig. S2): 9.05 ($\text{C}_{\text{Ar}}-\text{OH}$); 8.19–7.24 ($\text{C}_{\text{Ar}}-\text{H}$, phosphaphenanthrene); 6.79–6.63 ($\text{C}_{\text{Ar}}-\text{H}$, bisphenol A and monosubstituted benzene). ^{31}P nuclear magnetic resonance (^{31}P NMR, ppm, shown in Fig. S3): 38.24 and 37.40 (phosphaphenanthrene). Element content (Calculated/Experimental, wt.%): C, 72.86/72.93 \pm 0.15; H, 5.55/5.55 \pm 0.03.

2.3. Synthesis of cluster-like molecule TetraDSi

To avoid tetrachlorosilane hydrolysis, the 1, 2-dichloroethane (400 mL) was pre-distilled out 50 mL fraction by vacuum distillation at 100 °C. After that, DDBA (47.41 g, 0.064 mol) was firstly dissolved in pre-dehydrate 1, 2-dichloroethane with mechanical agitation at 85 °C. Then, cooling down to 30 °C, tetrachlorosilane (2.86 g, 0.0168 mol) was uniformly added into flask from rubber seal in 5–10 min, using injection syringe. The condensation reaction between DDBA and tetrachlorosilane was proceeded at 40 °C for 2 h firstly, and then at 90 °C for 20 h. The by-product hydrogen chloride was eliminated from condenser pipe, which was successively equipped with drying tube and absorption apparatus. After reaction finished, the solvent and residual hydrogen chloride were preliminarily removed via vacuum distillation at 100 °C. And then, the crude product was put in 180 °C vacuum oven to fully remove residual solvent and hydrogen chloride, forming brittle slight-yellow transparent



Scheme 1. Synthesis of cluster-like molecule TriDSi.

solid. The reaction formula of TetraDSi was shown in Scheme 2. Yield: above 98%. FTIR (cm^{-1} , shown in Fig. S1): 3404 and 3238 ($\text{C}_{\text{Ar}}-\text{OH}$); 3064 ($\text{C}_{\text{Ar}}-\text{H}$); 2963 and 2870 (CH_3); 2932 (CH_2); 1607, 1595, 1583, 1561, and 1498 (aromatic skeleton); 1431 ($\text{P}-\text{C}$); 1205 ($\text{P}=\text{O}$); 987 ($\text{Si}-\text{O}-\text{C}$); 915 ($\text{P}-\text{O}-\text{C}$); 755 (*o*-disubstituted benzene in phosphaphenanthrene). ^1H NMR (ppm, shown in Fig. S2): 9.04 ($\text{C}_{\text{Ar}}-\text{OH}$); 8.20–7.24 ($\text{C}_{\text{Ar}}-\text{H}$, phosphaphenanthrene); 6.78–6.62 ($\text{C}_{\text{Ar}}-\text{H}$, bisphenol A). ^{31}P NMR (ppm, shown in Fig. S3): 38.24 and 37.24 (phosphaphenanthrene). Element content (Calculated/Experimental, wt.%): C, 72.38/72.44 \pm 0.07; H, 5.53/5.63 \pm 0.05.

2.4. Preparation of epoxy thermosets

As reactive-type additive, the cluster-like molecules TriDSi and TetraDSi, and the contrastive DiDSi can all react with DGEBA, via the addition reaction between phenolic hydroxyl and epoxy group. Firstly, according to the formulas of epoxy thermosets listed in Table 1, DGEBA, DDM, and flame retardant additive (FR: DiDSi, TriDSi, or TetraDSi) were weighed accurately.

TriDSi-containing epoxy thermoset (TriDSi/EP): TriDSi was firstly

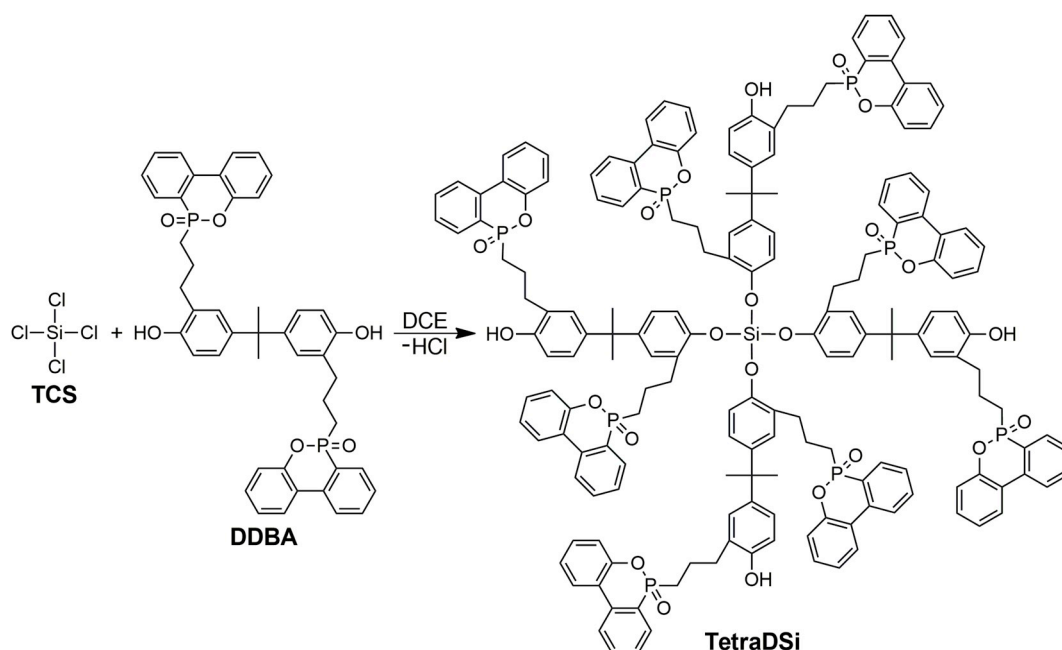
Table 1

Formulas of epoxy thermosets.

Samples	DGEBA (g)	DDM (g)	FR (g)	P (wt.%)	Si (wt.%)
EP	100	25.30	–	–	–
4%DiDSi/EP	100	24.99	5.21	0.30	0.07
4%TriDSi/EP	100	24.97	5.21	0.32	0.05
4%TetraDSi/EP	100	24.95	5.21	0.33	0.04
6%DiDSi/EP	100	24.82	7.97	0.45	0.10
6%TriDSi/EP	100	24.79	7.97	0.48	0.07
6%TetraDSi/EP	100	24.77	7.96	0.50	0.06

The phosphorus (P) and silicon (Si) contents of DiDSi/EP, TriDSi/EP, and TetraDSi/EP thermosets were also listed in Table 1.

dissolved into DGEBA with mechanical agitation at 140 °C. Then, the addition reaction between TriDSi and DGEBA was carried out for 1 h with the reaction accelerator benzyltriphenylphosphonium chloride (0.25% of DGEBA mass). After that, the curing agent DDM was added and dissolved into above mixture with mechanical agitation at 100 °C. After being degassed for 3 min in 120 °C vacuum oven, the uniform



Scheme 2. Synthesis of cluster-like molecule TetraDSi.

mixture was poured into preheated polytetrafluoroethylene molds, and precured at 120 °C for 2 h, and then fully cured at 170 °C for 4 h.

TetraDSi-containing epoxy thermoset (TetraDSi/EP): TetraDSi/EP was prepared via the same procedure as TriDSi/EP preparation.

DiDSi-containing epoxy thermoset (DiDSi/EP): DiDSi/EP was also prepared via the same procedure as TriDSi/EP preparation.

Neat epoxy thermoset (EP): The neat EP was prepared by the same preparation process of TriDSi/EP, without FR and reaction accelerator.

2.5. Characterization

Structural characterization: The chemical structures of cluster-like molecules TriDSi and TetraDSi were characterized and confirmed via FTIR, ¹H NMR, ³¹P NMR, and element content tests. FTIR spectrum was detected via potassium bromide discs by Nicolet iN10MX-type FTIR spectrometer, United States of America. ¹H NMR and ³¹P NMR spectra were obtained, using dimethyl sulfoxide-d₆ as deuterated solvent, via 700 MHz Bruker Avance III HD NMR spectrometer, Germany. Elemental content was measured on Vario EL elemental analyzer from Elementar Analysensysteme GmbH, Germany. The combustion temperature was at 900 °C, and the final elemental contents were the average value of two repeated tests.

Limited oxygen index (LOI) measurement: LOI value of epoxy thermoset was determined according to ASTM D2863, via Fire Testing Technology (FTT) Dynisco LOI instrument, United Kingdom. The dimension of specimen was 130.0 mm × 6.5 mm × 3.2 mm.

Vertical burning test: UL94 flammability classification of epoxy thermoset was measured according to ASTM D3801, using FTT UL94 flame chamber, United Kingdom. The dimension of specimen was 125.0 mm × 12.7 mm × 3.2 mm.

Cone calorimeter test: Combustion and charring behavior of epoxy thermoset were detected according to ISO 5660 under an external heat flux at 50 kW m⁻², by FTT cone calorimeter, United Kingdom. Each sample was tested twice. The dimension of specimen was 100 mm × 100 mm × 3 mm.

Unnotched Charpy impact test: Impact strength of epoxy thermoset was evaluated according to ISO 179-1 with a 2 J pendulum, using XJZ-50 digital impact test machine from Chengde testing machine Co. Ltd., China. The final impact strength was the average of five repeated tests. The dimension of specimen was 80 mm × 10 mm × 4 mm.

Differential scanning calorimeter (DSC) test: The glass transition temperature (*T_g*) of epoxy thermoset and the softening temperature of TriDSi and TetraDSi were determined under N₂ atmosphere via Q20 DSC produced by TA instruments, United States of America. The thermal history of TriDSi and TetraDSi were both eliminated at 170 °C for 5 min, then cooling down to 40 °C at a rate of 20 °C min and holding at 40 °C for 5 min, and then heating up to 170 °C at a rate of 20 °C min. The thermal history of epoxy thermoset was eliminated at 200 °C for 5 min, then cooling down to 40 °C at a rate of 20 °C min and holding at 40 °C for 5 min, and then heating up to 240 °C at a rate of 20 °C min.

Thermogravimetric (TG) test: The thermal decomposition of TriDSi, TetraDSi, and epoxy thermoset were analyzed on STA 8000 simultaneous thermal analyzer produced by PerkinElmer, Holland. The specimen was placed in alumina crucible. The thermal decomposition of TriDSi and TetraDSi were carried out under N₂ atmosphere, while epoxy thermoset was evaluated under N₂ and Air atmospheres, separately. Uniformly, the thermal decomposition procedures of TriDSi, TetraDSi, and epoxy thermoset were all carried out at a heating rate of 20 °C/min. Thermal stability of specimen was identified as the temperature at 1 wt % weight loss (*T_{d,1%}*).

Scanning electron microscope (SEM) test: The microstructures of impact fractured surface and charring residue were analyzed via Phenom ProX SEM produced by Phenom World, Holland. The working voltage was at 15 kV. The charring residue was sampled from the epoxy thermoset residue after cone calorimeter test.

TG-FTIR test: The thermal decomposition of epoxy thermoset was

carried out on STA 8000 simultaneous thermal analyzer produced by PerkinElmer, Holland. The specimen was placed in alumina crucible, and heated from 50 °C up to 700 °C at a rate of 20 °C/min under N₂ atmosphere. The real-time FTIR spectra of volatile products were monitored via a Frontier FTIR spectrometer produced by PerkinElmer, Italy. The FTIR specimen cell and transfer line were both kept at 280 °C.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) test: The pyrolysis of TriDSi and TetraDSi were separately detected by GCMS-QP 2010 Plus GC-MS with a PYR-4A pyrolyzer from Shimadzu, Japan. The helium was utilized as carrier gas. The pyrolysis temperature was at 500 °C.

3. Results and discussion

3.1. Anti-impact performance of epoxy thermosets

The reactive phenolic hydroxyl groups, in cluster-like molecules, make both TriDSi and TetraDSi be able to link into the cross-linked network of epoxy thermoset. The former research regarding DiDSi-toughening epoxy thermoset disclosed that, phosphaphenanthrene/siloxane bigroup segmer constituted an effective toughening unit, for the synergy between above two groups in toughening epoxy thermoset [51]. Then, as shown in Fig. 2, compared with the contrastive DiDSi, TriDSi and TetraDSi can construct more interlinked toughening segmers (phosphaphenanthrene/siloxane bigroup segmer) with thermoset matrix in each toughening unit, for their higher level of reactive group quantity. Therefore, as components of the covalent bond structure in thermoset network, the larger-size cluster-like molecules TriDSi and TetraDSi, owning branched aggregation of toughening segmers in greater degree, perhaps paly greater influence on the fracture toughness of thermoset matrix.

As the results shown in Fig. 3, TriDSi/EP and TetraDSi/EP thermosets all achieved obviously higher impact strength, compared with neat EP. And, in both TriDSi/EP and TetraDSi/EP thermosets, their impact strength values were positively correlated with the addition amount of TriDSi or TetraDSi. It indicates that, TriDSi and TetraDSi are both capable of endowing epoxy thermoset with higher anti-impact performance effectively. More importantly, at the same addition level, the impact strength of TriDSi/EP and TetraDSi/EP were both higher than that of DiDSi/EP, implying that TriDSi and TetraDSi were more efficient than DiDSi in toughening epoxy thermoset. Namely, the larger-size cluster-like molecule, with more toughening segmers aggregating together, performed higher-efficiency toughening action. Hence, it can be deduced that, besides the former reported phosphaphenanthrene/siloxane bigroup synergy in toughening epoxy thermoset [51], as the schematic diagram shown in Fig. 2, with the increase of cluster-like molecule size, more toughening segmers aggregated in single molecule, which further endowed cluster-like bigroup molecules with higher toughening efficiency.

As for the impact strength of 6%TriDSi/EP being larger than that of 6%TetraDSi/EP, it is the result of the compromise between the local centralized toughening and the distribution density of toughening units. Namely, the toughening efficiency of cluster-like molecule is influenced by both of above two factors. At the same addition level, compared with 6%TetraDSi/EP, 6%TriDSi/EP contained less toughening segmers in each local toughening unit. However, for the reason of lower molecular weight, TriDSi achieved higher distribution density in 6%TriDSi/EP instead. The research results indicated that, in the case of 6%TriDSi/EP, the compromise of above two factors achieved higher toughening efficiency.

Furthermore, to further know about the detailed influence of incorporated TriDSi and TetraDSi on the fracture of thermoset matrix, the microstructure for the fractured surface of epoxy thermoset was also observed via SEM. As shown in Fig. 4, unlike the fractured surface of neat EP with lots of lamellar fracture marks, there are massive laniated and warping fracture traces throughout the fractured surface of both 6%

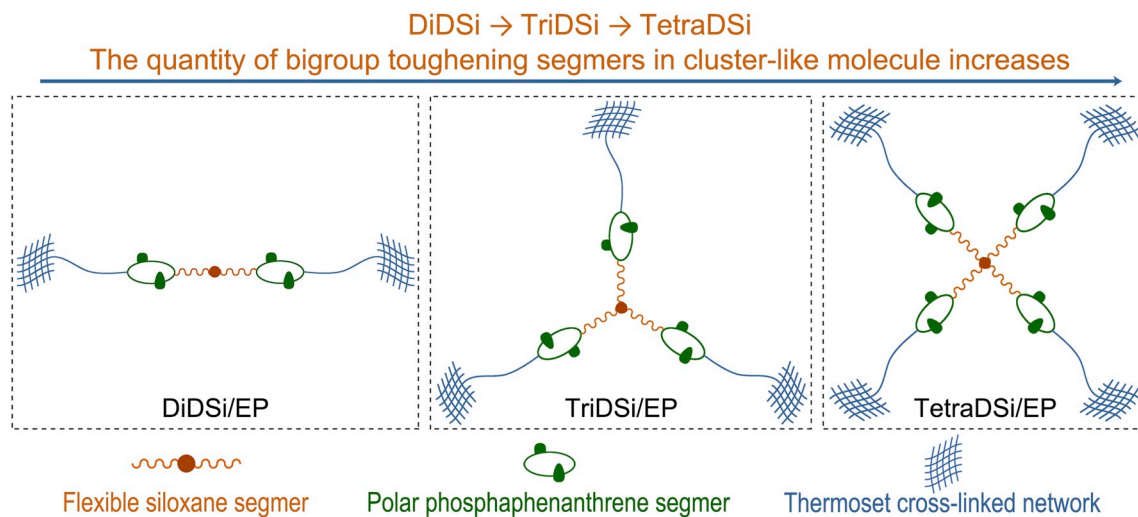


Fig. 2. Schematic diagram of cluster-like molecule in epoxy thermosets.

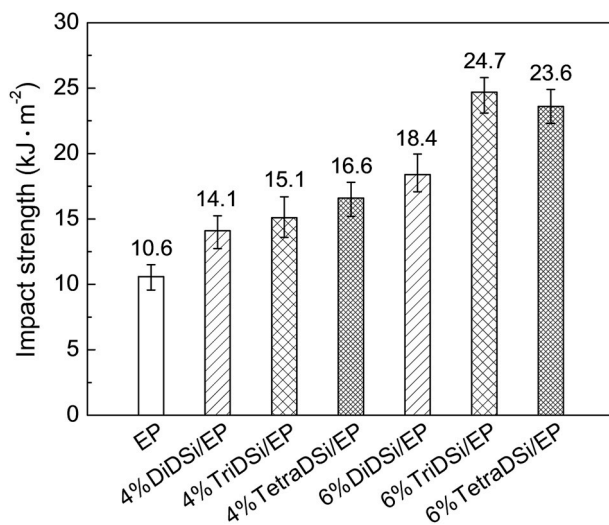


Fig. 3. Impact strength of epoxy thermosets.

TriDSi/EP and 6%TetraDSi/EP. Obviously, among the same cross-sectional area, compared with the relatively flat lamellar fracture path, the much more rugged fracture path possessed larger fracture area, which should be formed by consuming more impact energy. Therefore, it can be concluded that, during fracturing, the toughening action of phosphaphenanthrene/siloxane segmer, in both TriDSi/EP and TetraDSi/EP, induced thermoset matrix to experience more complex, tanglier, and larger-area fracture path with larger amount of impact energy consumption, and then brought thermoset matrix higher fracture toughness.

Besides, the laniated and warping fracture traces on the fracture surface of 6%TriDSi/EP and 6%TetraDSi/EP are both relatively more massive, intensive, and crowded than that of 6%DiDSi/EP. It signifies that, 6%TriDSi/EP and 6%TetraDSi/EP should both experience relatively larger-area fracture path than 6%DiDSi/EP. That is why the impact strength of 6%TriDSi/EP and 6%TetraDSi/EP were both higher than that of 6%DiDSi/EP. As for the distinction between 6%TriDSi/EP and 6%TetraDSi/EP, due to their less difference in impact strength, their fracture morphology was too close to distinguish their difference clearly, for the imprecise qualitative characteristic of fracture traces. Anyway, it can be concluded that, the branched aggregation of toughening segmers in cluster-like molecules induced epoxy thermoset to fracture along

more complex and larger-area path, realizing superior fracture toughness.

3.2. Anti-ignition and self-extinguishing performance of epoxy thermosets

In estimating the combustibility of materials, the ignitability and self-extinguishing performance are both crucial assessment indexes. To evaluate the influence of cluster-like molecules TriDSi and TetraDSi on the ignitability and self-extinguishing performance of epoxy thermoset, the LOI and UL94 rating of TriDSi/EP and TetraDSi/EP thermosets were detected via LOI measurement and vertical burning test.

As the results listed in Table 2, the incorporated TriDSi and TetraDSi both elevated the LOI and UL94 rating of epoxy thermoset markedly, endowing thermoset matrix with excellent anti-ignition and self-extinguishing performance. In detail, at only 4 wt% addition level, TriDSi and TetraDSi improved the LOI of epoxy thermoset from 26.4% up to 33.4% and 34.6%, separately. Moreover, the LOI value of modified epoxy thermoset still increased with the increasing addition amount of cluster-like molecules. Meanwhile, compared with the contrastive DiDSi/EP, at the same addition level, the LOI value of modified epoxy thermoset increased with the increasing phosphaphenanthrene group quantity and P content of cluster-like molecules. Hence, combining the results in former research, besides the influence of P content and P/Si synergy [51], the group aggregation effect from cluster-like molecules also contributed great to elevating the LOI of epoxy thermoset.

Furthermore, 6%TriDSi/EP and 6%TetraDSi/EP both passed UL94 V-0 rating, while the contrastive 6%DiDSi/EP only met the requirement of UL94 V-1 rating, for its overlong after-flame time. Therefore, it can be inferred that, the aggregation of phosphaphenanthrene groups in cluster-like molecules still further enhanced their free radical quenching effect, which endowed 6%TriDSi/EP and 6%TetraDSi/EP with more excellent self-extinguishing performance.

3.3. Flame retardant behavior of epoxy thermosets in cone calorimetry

To further explore more detailed influence of cluster-like molecules TriDSi and TetraDSi on the combustion behavior of epoxy thermoset, cone calorimeter was also adopted to detect and collect the combustion parameters of burning 6%TriDSi/EP and 6%TetraDSi/EP thermosets.

As the heat release rate (HRR) curves shown in Fig. 5, it can be observed that, the incorporated TriDSi and TetraDSi not only suppressed the combustion growth of ignited epoxy thermoset, but also inhibited the combustion intensity of thermoset matrix to a significantly lower level. In detail, as the typical parameters listed in Table 3, the peak of

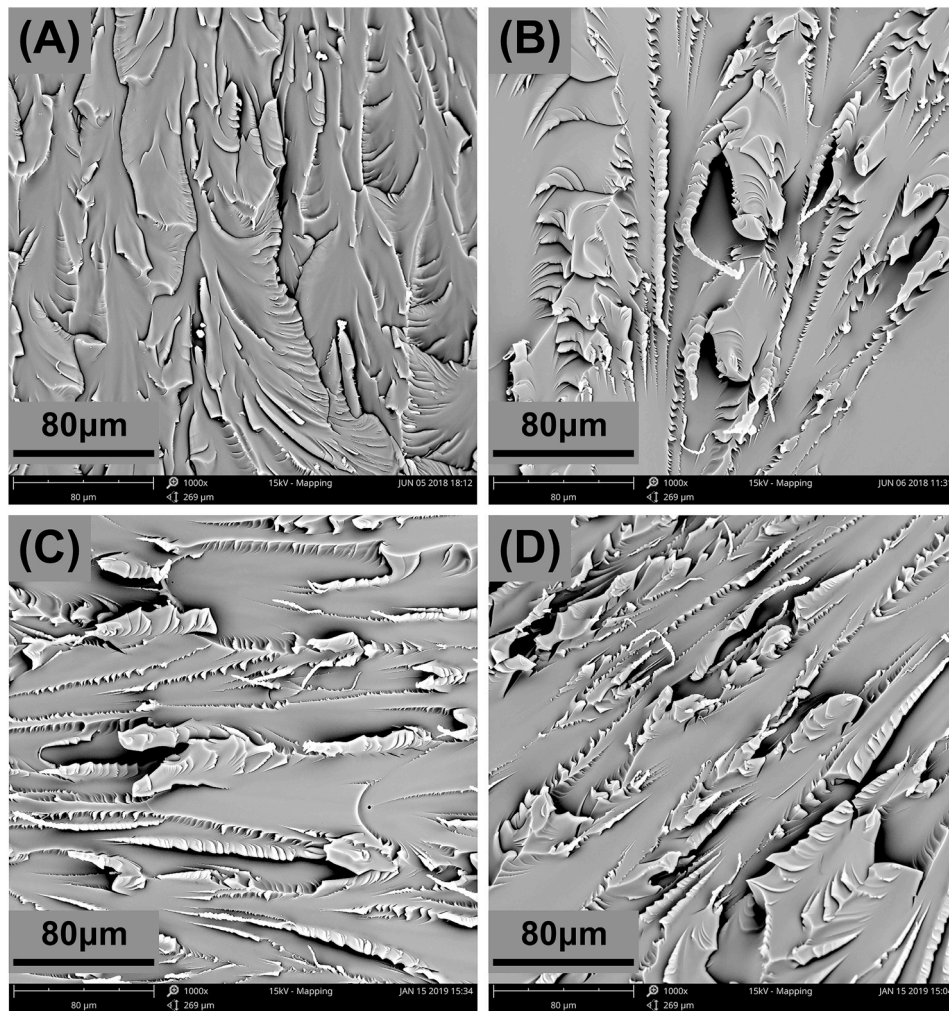


Fig. 4. Microstructure for the fractured surface of epoxy thermoset after impact test (SEM-1000X). (A) EP, (B) 6%DiDSi/EP, (C) 6%TriDSi/EP, and (D) 6%TetraDSi/EP.

Table 2
LOI and UL94 rating of epoxy thermosets.

Samples	LOI (%)	Vertical burning test			
		After-flame time		UL94 Rating	Dripping
		t_1^- (s)	t_2^- (s)		
EP	26.4	83.0 ^a	–	Unrated	No
4%DiDSi/EP	32.4	12.8	9.2	V-1	No
4%TriDSi/EP	33.4	8.1	10.5	V-1	No
4%TetraDSi/EP	34.6	11.5	9.0	V-1	No
6%DiDSi/EP	34.1	8.2	7.1	V-1	No
6%TriDSi/EP	35.2	5.2	3.5	V-0	No
6%TetraDSi/EP	36.0	3.0	2.4	V-0	No

^a The combustion flame spread to specimen clamp in the first flame application.

HRR (pk-HRR) in 6%TriDSi/EP and 6%TetraDSi/EP were both much lower than that of neat EP. Moreover, compared with the contrastive 6%DiDSi/EP, the order is $\text{pk-HRR}_{6\%TetraDSi/EP} < \text{pk-HRR}_{6\%TriDSi/EP} < \text{pk-HRR}_{6\%DiDSi/EP}$. It indicates that, with more and more phosphaphenanthrene group aggregating in one molecule, the cluster-like molecules suppressed the combustion intensity of epoxy thermoset more efficiently.

Noteworthy, the HRR curves in Fig. 5 still revealed that, compared with 6%TriDSi/EP and 6%TetraDSi/EP, there is an extra heat release

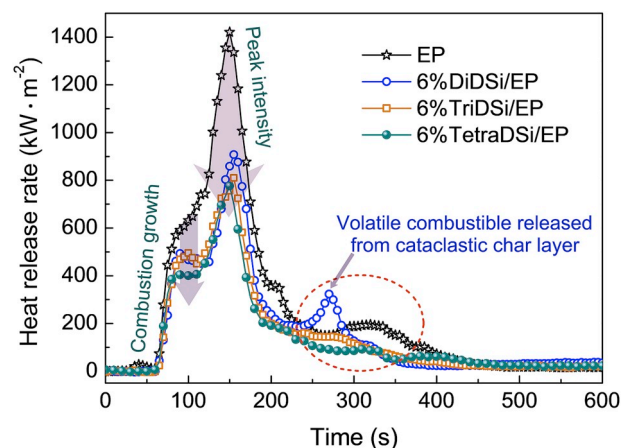


Fig. 5. HRR curves of epoxy thermosets.

peak appearing on the late-stage HRR curve of 6%DiDSi/EP. This extra heat release peak should be mainly ascribed to the deficiency of charring barrier in burning 6%DiDSi/EP. Videlicet, under continuous thermal radiation (50 kW m^{-2}), the insufficient thermo-oxidative stability of 6%DiDSi/EP residue made its charring barrier to be broken more easily, which resulted in that, the encapsulated volatile combustibles escaped

Table 3

Typical parameters of epoxy thermostets from cone calorimetry.

Samples	TTI (s)	pk-HRR (kW·m ⁻²)	av-EHC (MJ·kg ⁻¹)	THR (MJ·m ⁻²)	TSP (m ²)	av-COY (kg·kg ⁻¹)	av-CO ₂ Y (kg·kg ⁻¹)	R _{600s} (wt.%)
EP	56 ± 1	1420 ± 53	29.9 ± 0.3	144 ± 5	52.2 ± 2.1	0.13 ± 0.01	2.51 ± 0.10	7.7 ± 0.2
6%DiDSi/EP	55 ± 2	907 ± 8	22.6 ± 0.2	101 ± 1	48.8 ± 0.2	0.13 ± 0.01	1.76 ± 0.02	14.1 ± 0.3
6%TriDSi/EP	58 ± 0.5	810 ± 26	21.4 ± 0.2	90 ± 1	43.0 ± 0	0.12 ± 0.01	1.70 ± 0.01	13.2 ± 0.1
6%TetraDSi/EP	57 ± 0.5	776 ± 5	19.9 ± 0.8	83 ± 3	45.5 ± 1.6	0.11 ± 0.01	1.63 ± 0.04	13.7 ± 0.2

from broken char layer, and burnt intensively, forming other heat release peak. As for the charring barrier of burning 6%TriDSi/EP and 6% TetraDSi/EP, their persistent and effective barrier effect on heat, oxygen, and volatiles exchange disclosed the higher-quality barrier layer with better thermo-oxidative stability. Therefore, it can be concluded that, compared with DiDSi, the higher-level phosphaphenanthrene group aggregation in cluster-like molecules further forced thermostet matrix to forming more thermo-oxidative stable charring barrier, which endowed burning epoxy thermostet with more effective barrier and protective effect.

The residue retention (R_{600s}, at 600s) listed in Table 3 also disclosed that, compared with neat EP, 6%TriDSi/EP and 6%TetraDSi/EP both achieved stronger charring ability. In detail, the R_{600s} of 6%TriDSi/EP and 6%TetraDSi/EP increased separately by 5.5 wt% and 6.0 wt%, compared with that of neat EP. Meanwhile, 6%TriDSi/EP and 6%TetraDSi/EP both achieved much lower average effective heat of combustion (av-EHC) than the case of neat EP, signifying that TriDSi and TetraDSi both brought epoxy thermostet more effective gas-phase flame retardant effect. Furthermore, compared with the contrastive 6%DiDSi/EP, the order is av-EHC_{6%TetraDSi/EP} < av-EHC_{6%TriDSi/EP} < av-EHC_{6%DiDSi/EP}, indicating that the higher-level phosphaphenanthrene group aggregation in cluster-like molecules produced stronger gas-phase inhibition effect. Since siloxane group mainly acted in condensed phase, the stronger gas-phase flame retardant effect of TriDSi and TetraDSi should be mostly ascribed to the higher P content and the aggregation

effect of phosphaphenanthrene groups, which contributed to the intensive release of gas-phase quenching effect from phosphaphenanthrene groups. As for the decrease of total smoke production (TSP), average carbon monoxide yield (av-COY), and average carbon dioxide yield (av-CO₂Y) in modified epoxy thermostet, it can be ascribed to the joint actions of cluster-like molecules in both gas and condensed phases.

In addition, the time to ignition (TTI) listed in Table 3 also reveals that, whether 6%TriDSi/EP or 6%TetraDSi/EP, their TTI values were both almost the same as that of neat EP. Thus, it can be concluded that, once the cluster-like molecules TriDSi and TetraDSi were embedded in epoxy thermostet, becoming components of cross-linked network, they both influenced less on the thermal stability of thermostet matrix.

3.4. Charring behavior of epoxy thermostets

Generally, the condensed-phase flame retardant effect plays a direct influence on the charring behavior of burning materials. To reveal how cluster-like molecules TriDSi and TetraDSi influenced the charring behavior of burning epoxy thermostet, as shown in Fig. 6, the surface residue of epoxy thermostet after cone calorimeter test was scanned via SEM.

As the outer-side microtopography of surface residue shown in Fig. 6 (A), it can be observed that, as similar as the case of 6%DiDSi/EP, the burnt 6%TriDSi/EP and 6%TetraDSi/EP formed dense and compact charring layer with many solid particles spreading on the surface of

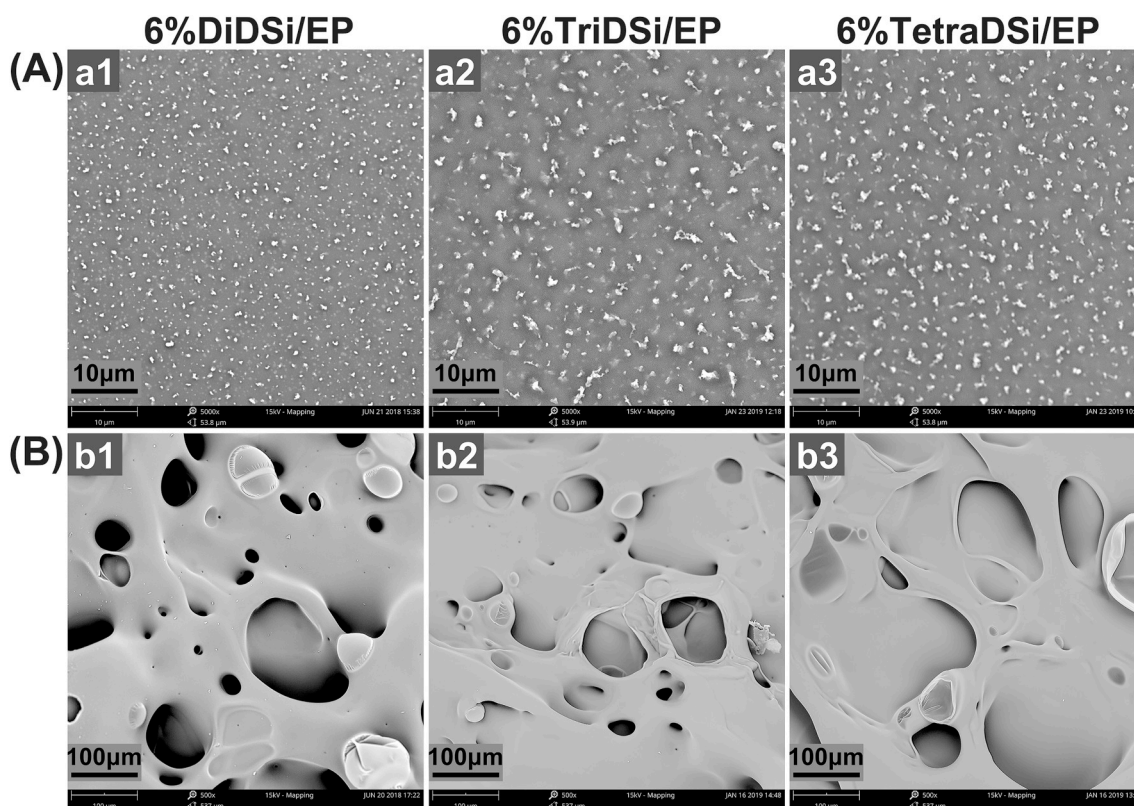


Fig. 6. The surface residue of epoxy thermostets after cone calorimeter test. (A) Outer-side microtopography (SEM-5000X); (B) Inner-side microtopography (SEM-500X).

residue. According to the results reported in former research, these solid particles, spreading on the surface of 6%DiDSi/EP residue, belonged to silicon oxide particles, which possessed excellent thermo-oxidative stability, and contributed to further improving the thermal stability of phosphorus-containing residue [51]. Since DiDSi, TriDSi, and TetraDSi all possessed basically similar chemical groups, it can be analogized that, the solid particles spreading on the surface of 6%TriDSi/EP and 6% TetraDSi/EP residue shall also belong to the thermo-oxidative stable silicon oxide particles, migrating and enriching from the pyrolyzed siloxane groups in incorporated TriDSi and TetraDSi. Noteworthy, with higher-level phosphaphenanthrene group aggregation, the larger-size cluster-like molecules TriDSi and TetraDSi also produced bigger silicon oxide particles than DiDSi during the combustion of epoxy thermoset. It is mainly because of the lower Si content in 6%TriDSi/EP and 6%TetraDSi/EP, which made the silicon oxide from decomposed TriDSi and TetraDSi agglomerate more easily.

Furthermore, the inner-side microtopography of surface residue shown in Fig. 6(B) reveals that, there are many unbroken and sealed bubble films spreading on the inner side of the surface residue from 6%TriDSi/EP and 6%TetraDSi/EP. According to the former reported researches [37], these bubble films should come from the phosphorus-containing viscous residue of phosphaphenanthrene-containing epoxy thermoset. Nevertheless, unlike the relatively dense and compact inner-side structure of the surface residue from 6%TriDSi/EP and 6%TetraDSi/EP, there are many opening channels imbedded in the inner side of the surface residue from 6%DiDSi/EP. Thus, once outer-side charring layer is broken, these opening channels shall become relatively fluent path for heat, oxygen, and volatiles exchange, which is disadvantageous to the barrier and protective effect of char layer. This is the main reason to the appearance of extra heat release peak on the late-stage HRR curve of 6%DiDSi/EP. Namely, when outer-side charring layer of 6%DiDSi/EP was broken for continuous thermal radiation, the encapsulated volatile combustibles were easily to escape from aforementioned opening channels quickly, and burnt intensively.

Consequently, it can be concluded that, the excellent charring barrier of burning 6%TriDSi/EP and 6%TetraDSi/EP were formed under the joint effect of phosphaphenanthrene and siloxane groups in cluster-like molecules. And, the higher-level phosphaphenanthrene group aggregation made cluster-like molecules be more capable to facilitate epoxy thermoset forming higher-quality dense and thick charring barrier, bringing burning thermoset matrix more effective condensed-phase flame retardant effect.

3.5. Thermal and decomposition behavior of epoxy thermosets

During combustion, besides charring ability, the thermal stability and decomposition behavior of materials also influence greatly on their burning behavior. To further disclose and confirm how cluster-like

molecules TriDSi and TetraDSi suppressed the combustibility of epoxy thermoset, the thermal, decomposition, and charring parameters of 6% TriDSi/EP and 6%TetraDSi/EP were measured via TG test. Meanwhile, the T_g of 6%TriDSi/EP and 6%TetraDSi/EP were also detected by DSC test, to estimate the influence of TriDSi and TetraDSi on the softening temperature of epoxy thermoset.

As shown in Fig. 7, in initial decomposition stage, the TG curves of 6%TriDSi/EP and 6%TetraDSi/EP showed little difference with that of neat EP. In detail, as the $T_{d,1\%}$ listed in Table 4, the $T_{d,1\%}$ value of 6% TriDSi/EP and 6%TetraDSi/EP decreased by 6 °C and 4 °C, separately, compared with that of neat EP in N₂ atmosphere, while the $T_{d,1\%}$ value of 6%TriDSi/EP and 6%TetraDSi/EP both increased by 16 °C than that of neat EP in air atmosphere. This result reveals that, the incorporated TriDSi and TetraDSi did not influence the thermal stability of epoxy thermoset too much, consisting with the results of TTI in cone calorimeter test. It can be ascribed to the good inherent thermal stability (shown in Fig. S4) and especially the reactive feature of cluster-like molecules TriDSi and TetraDSi, which enabled them to be linked into thermoset cross-linking network with less unstable structure.

Even so, in both N₂ and air atmospheres, the maximum mass loss rate (MLR_{max}) values of 6%TriDSi/EP and 6%TetraDSi/EP were both obviously lower than that of neat EP. It indicates that, the incorporated TriDSi and TetraDSi restrained the decomposition of epoxy thermoset, which reduced the release rate of decomposition volatiles. It is advantageous to lower down the burning intensity of thermoset matrix, because of the weakened fuel supply. Meanwhile, the MLR_{max} values of 6%TriDSi/EP and 6%TetraDSi/EP were still lower than that of the contrastive 6%DiDSi/EP. Therefore, it can be concluded that, with higher-level phosphaphenanthrene group aggregation, the cluster-like molecules TriDSi and TetraDSi inhibited the decomposition rate of epoxy thermoset more efficiently.

Moreover, in both N₂ and air atmospheres, the residue retentions (R_{700°C}, at 700 °C; R_{800°C}, at 800 °C.) of 6%TriDSi/EP and 6%TetraDSi/EP were both visibly larger than that of neat EP, suggesting that the incorporated TriDSi and TetraDSi both facilitated more matrix composition to be reserved in condensed phase. Especially for the range of 700–800 °C under air atmosphere, the order of mass loss (ML) of thermoset residue is ML_{6%DiDSi/EP} (9.7 wt%) > ML_{6%TriDSi/EP} (8.5 wt%) > ML_{6%TetraDSi/EP} (8.3 wt%). According to this result, within this stage, the order for the thermal stability of thermoset residue can be disclosed as 6%TetraDSi/EP > 6%TriDSi/EP > 6%DiDSi/EP. Consequently, although the former research disclosed that, the joint action of phosphaphenanthrene and siloxane groups forced burning thermoset to forming high-quality charring barrier [51], the increase of phosphaphenanthrene/siloxane specific value and the aggregation of phosphaphenanthrene group in cluster-like molecule still contributed to further improve the charring capability of thermoset matrix, making more thermoset components be reserved in condensed-phase charring

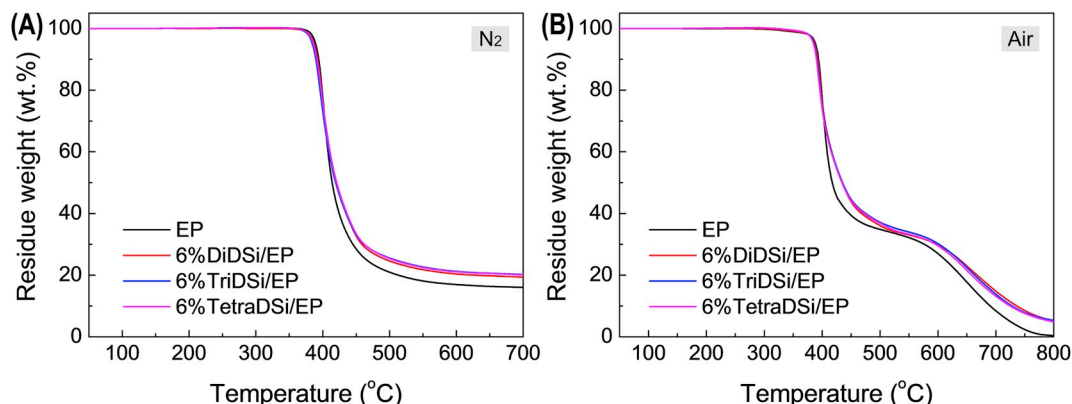


Fig. 7. TG curves of epoxy thermosets. (A) N₂ atmosphere; (B) Air atmosphere.

Table 4
Thermal, decomposition, and charring parameters of epoxy thermosets.

Samples	T_g (°C)	N ₂ atmosphere			Air atmosphere			
		$T_{d,1\%}$ (°C)	MLR _{max} (%·min ⁻¹)	R _{700°C} (wt.%)	$T_{d,1\%}$ (°C)	MLR _{max} (%·min ⁻¹)	R _{700°C} (wt.%)	R _{800°C} (wt.%)
EP	166	379	48.8	16.0	348	45.4	8.4	0.4
6%DiDSi/EP	167	375	40.2	19.3	357	38.1	14.8	5.1
6%TriDSi/EP	167	373	35.0	20.2	364	37.8	13.8	5.3
6%TetraDSi/EP	168	375	35.2	20.1	364	37.0	13.2	4.9

residue. It is consistent with the charring behavior of modified epoxy thermoset, disclosed from cone calorimeter and SEM tests.

As for the T_g of epoxy thermosets, the results shown in Table 4 reveal that, whether 6%TriDSi/EP, 6%TetraDSi/EP, or the contrastive 6% DiDSi/EP, their T_g values were all quite close to that of neat EP. Therefore, it can be confirmed that, the incorporated cluster-like molecules TriDSi and TetraDSi do not reduce the softening temperature of epoxy thermoset.

3.6. Real-time tracing on the volatiles of decomposing epoxy thermosets

During decomposition, the volatiles from material also reflect important working traces of flame retardant behavior. For this reason, the real-time FT-IR spectra of the volatiles from decomposing 6%TriDSi/EP and 6%TetraDSi/EP were traced via TG-FTIR test, respectively.

As shown in Fig. 8, for 6%TriDSi/EP and 6%TetraDSi/EP, the main absorption peaks of their volatiles were basically the same as that of neat EP in peak position. It indicates that, the incorporated cluster-like molecules TriDSi and TetraDSi both influenced less on the major structural features of the volatiles from decomposing thermoset matrix. As for the weakened absorption peaks in Fig. 8(B) and (C), it indicates that the incorporated TriDSi and TetraDSi both reduced the quantity of the volatiles from decomposing matrix. It is consistent with the reduced MLR_{max} of modified epoxy thermoset in TG test.

In detail, as shown in the shadowed (a), (b), and (c) regions, for 6% TriDSi/EP and 6%TetraDSi/EP, the peaks of their volatiles at 2976 cm⁻¹ (aliphatic C–H), 1818–1663 cm⁻¹ (carbonylic C=O), and 828 cm⁻¹ (para-disubstituted benzene C–H) were all obviously lower than those of the volatiles from neat EP. Among them, the aliphatic and carbonylic fragments all burn easily, belonging to the important fuels of combustion reaction, especially the extremely flammable carbonylic fragments.

Hence, it can be concluded that, the suppressing effect of TriDSi and TetraDSi on the decomposition of thermoset matrix weakened the fuel supply of combustion process, promoting the reduction of heat release from burning epoxy thermoset.

3.7. Pyrolysis behavior of cluster-like molecules TriDSi and TetraDSi

Actually, in burning modified epoxy thermoset, all flame retardant effects were carried out directly by the pyrolytic products of cluster-like molecules TriDSi and TetraDSi. Therefore, the analysis on the pyrolysis behavior of TriDSi and TetraDSi is also beneficial greatly to elucidating their working mode in flame retarding epoxy thermoset.

According to the MS spectra shown in Fig. S6, the pyrolytic products of the cluster-like molecule TriDSi can be summarized into the following three parts: (1) benzene (M78) from phenylsiloxane segment; (2) phenolic fragments (M108, M134, M150, M160, and M174) from bisphenol-A segment; (3) phosphaphenanthrene fragments (M230 and M242) and phenanthrene (M178) from phosphaphenanthrene segment. Thereinto, phenanthrene is the pyrolytic by-product of phosphaphenanthrene group after releasing PO radicals. Based on above MS results, the presumptive pyrolysis route of TriDSi was deduced out and shown in Fig. 9.

Similarly, according to the MS spectra shown in Fig. S7, the pyrolytic products of the cluster-like molecule TetraDSi can be divided into the following two parts: (1) phenolic fragments (M108, M134, M150, M160, M174, and M176) from bisphenol-A segment; (2) phosphaphenanthrene fragments (M230 and M242), o-phenylphenol (M170), and phenanthrene (M178) from phosphaphenanthrene segment. Thereinto, o-phenylphenol and phenanthrene both belong to the pyrolytic by-products of phosphaphenanthrene group after releasing PO free radicals. Then, the presumptive pyrolysis route of TetraDSi were concluded and shown in

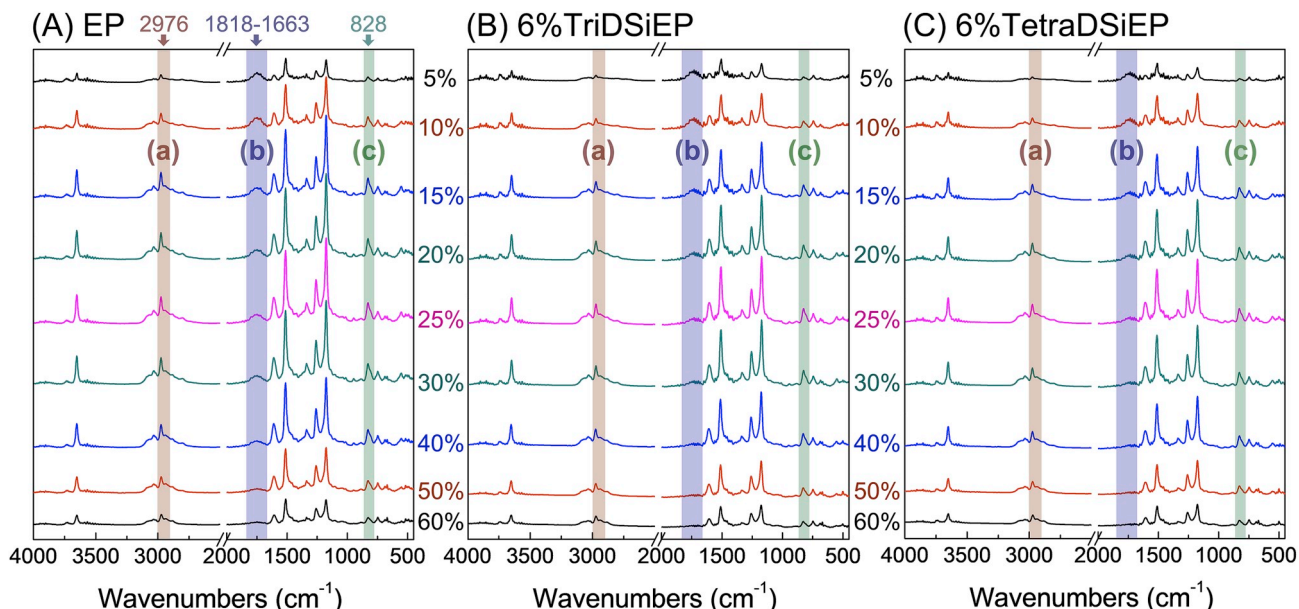


Fig. 8. FTIR spectra for the volatiles of decomposing epoxy thermosets within 60 wt% mass loss. (A) EP; (B) 6%TriDSi/EP; (C) 6%TetraDSi/EP.

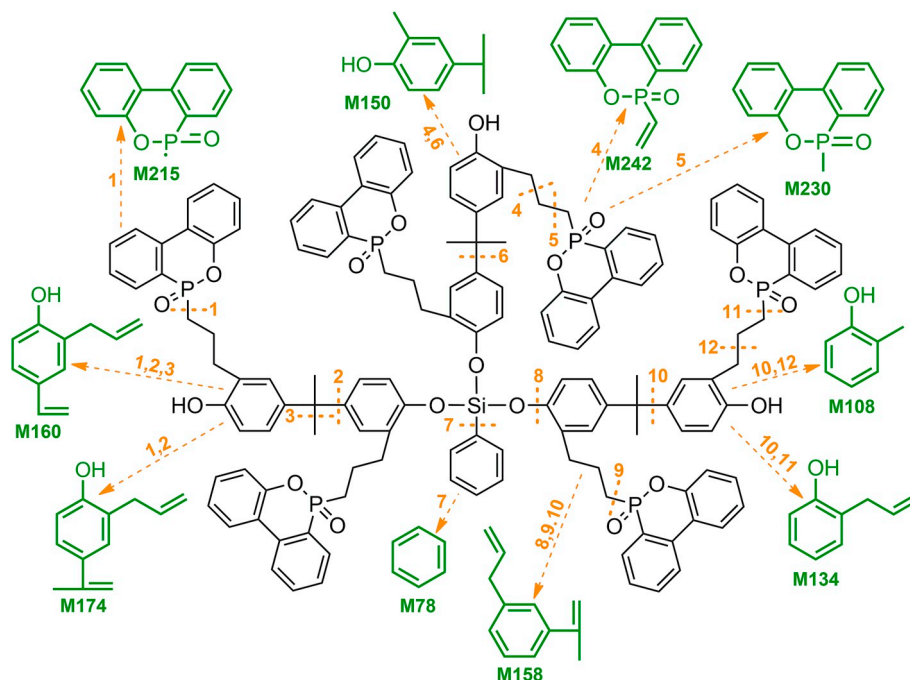


Fig. 9. Presumptive pyrolysis route of cluster-like molecule TriDSi.

Fig. 10.

Observably, the pyrolysis of TriDSi and TetraDSi both released massive phosphaphenanthrene-containing fragments (M230 and M242) at 500 °C pyrolysis temperature. During combustion, these phosphaphenanthrene-containing fragments would be pyrolyzed further, releasing its gas- and condensed-phase flame retardant effects. To reveal this process, according to the MS spectra of M230 and M242

fragments shown in Figs. S6 and S7, the presumptive pyrolysis routes of aforementioned phosphaphenanthrene-containing fragments were ratiocinated and shown in Fig. 11. The pyrolysis routes reveal that, the further pyrolysis of M230 and M242 fragments produced many PO (M47, M63, and M139) and phenoxy (M93) free radicals, which are capable of quenching the vital active free radicals in combustion reaction, like H and OH free radicals. For the free radical quenching effect of

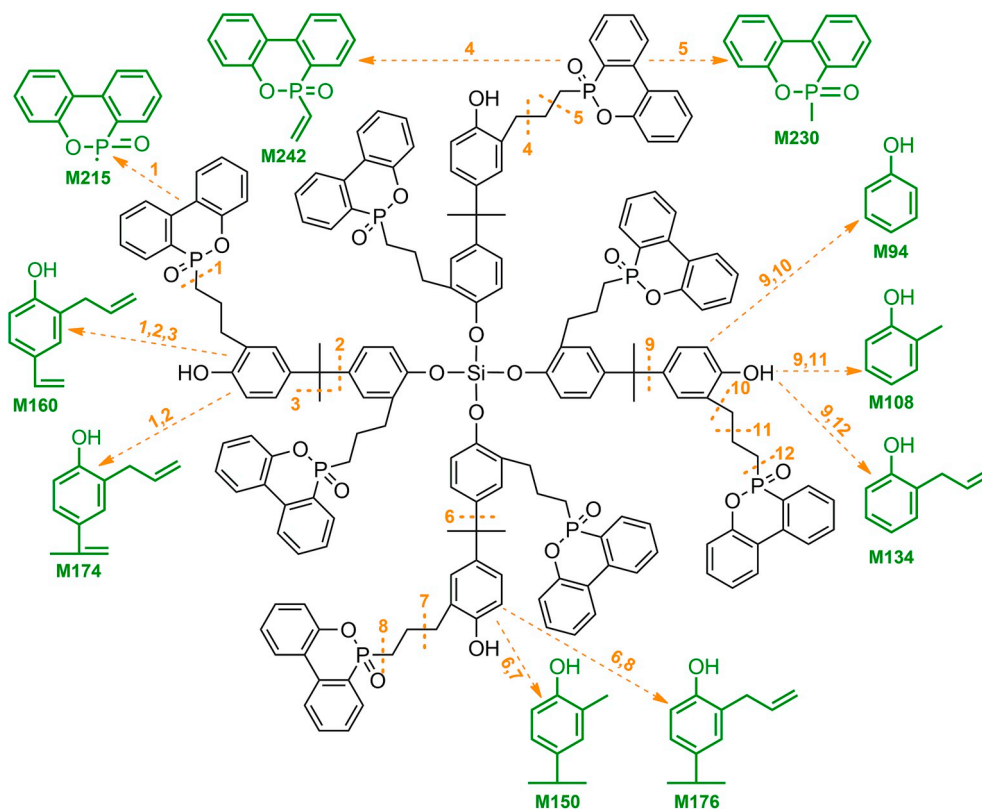


Fig. 10. Presumptive pyrolysis route of cluster-like molecule TetraDSi.

PO and phenoxy radicals, the vital free radical reactions of burning thermoset matrix can be suppressed or even terminated, endowing epoxy thermoset with good flame retardant performance, such as anti-ignition and self-extinguishing performance.

3.8. Toughening and flame retardant mechanisms of cluster-like molecules TriDSi and TetraDSi

The researches on the impact strength and flame retardant properties of TriDSi/EP and TetraDSi/EP thermosets revealed that, the incorporated TriDSi and TetraDSi improved the fracture toughness and lowered the combustibility of thermoset matrix effectively, endowing epoxy thermoset with outstanding anti-impact and flame retardant performance, simultaneously.

In the aspect of toughening behavior, compared with DiDSi/EP reported in former research [51], TriDSi/EP and TetraDSi/EP possessed very similar but superior toughening effect. Similarly, after incorporating TriDSi and TetraDSi, the flexible siloxane segment played vital roles in toughening thermoset matrix, while the concomitant polar phosphaphenanthrene-containing segment further assisted siloxane segment to realize higher-efficiency toughening effect. The difference is that, the higher-level aggregated phosphaphenanthrene/siloxane toughening segments brought TriDSi and TetraDSi higher-efficiency toughening effect.

In the aspect of flame retardant behavior, the gas- and condensed-phase effects of phosphaphenanthrene group played crucial roles in suppressing the combustion of epoxy thermoset. Especially, the aggregation of phosphaphenanthrene group brought cluster-like molecule higher-efficiency gas-phase flame retardant effect.

On one hand, the pyrolytic products of aggregated phosphaphenanthrene groups intensively interplayed with thermoset matrix, which not only inhibited the decomposition speed of matrix more effectively, but also facilitated more matrix composition to be reserved in condensed phase as phosphorus-containing residue, weakening and reducing the fuel supply of combustion reaction. On the other hand, the pyrolysis of phosphaphenanthrene-containing segments also intensively released massive PO and phenoxy free radicals, which quenched the indispensable active free radicals (such as H and OH free radicals), suppressing or even terminating the free radical reactions of burning thermoset matrix.

Meanwhile, the pyrolysis of siloxane group from cluster-like molecule formed thermo-oxidative stable silicon oxide particles, which combined with phosphorus-containing residue to form dense and thick phosphorus/silicon-containing residue with higher thermo-oxidative stability, endowing burning thermoset matrix with more effective barrier and protective effect.

4. Conclusion

Two kinds of cluster-like molecules TriDSi and TetraDSi were synthesized and confirmed structurally. The incorporated TriDSi and TetraDSi both improved the anti-impact property and lowered the combustibility of epoxy thermoset, simultaneously. The impact strength of 6%TriDSi/EP and 6%TetraDSi/EP increased by 133% and 123%, separately, compared with that of neat EP. With more phosphaphenanthrene/siloxane bigroup toughening segments aggregating in one molecule, the toughening efficiency of cluster-like molecule increased visibly. Meanwhile, 6%TriDSi/EP and 6%TetraDSi/EP both passed UL94 V-0 rating with a LOI value of 35.2% and 36.0%, separately. Moreover, the pk -HRR, av -EHC, and THR of 6%TetraDSi/EP decreased by 45.4%, 33.4%, and 42.4%, respectively, in contrast to those of neat EP. With phosphaphenanthrene group aggregating and phosphaphenanthrene/siloxane specific value increasing, the cluster-like molecules suppressed decomposition speed, improved charring capability, and quenched active free radicals more efficiently, in burning epoxy thermoset. Furthermore, the co-action of phosphaphenanthrene and siloxane groups, in the cluster-like molecules with higher-level aggregation, promoted the burning thermoset to forming higher-quality charring barrier, endowing epoxy thermoset with more sustained and effective barrier and protective effect. Through the aggregation effect in toughening and flame retardant behavior, the cluster-like molecules endowed epoxy thermoset superior fracture toughness and flame retardant properties, providing a promising choice for advanced epoxy thermoset manufacture.

Declaration of competing interest

There are no conflicts to declare.

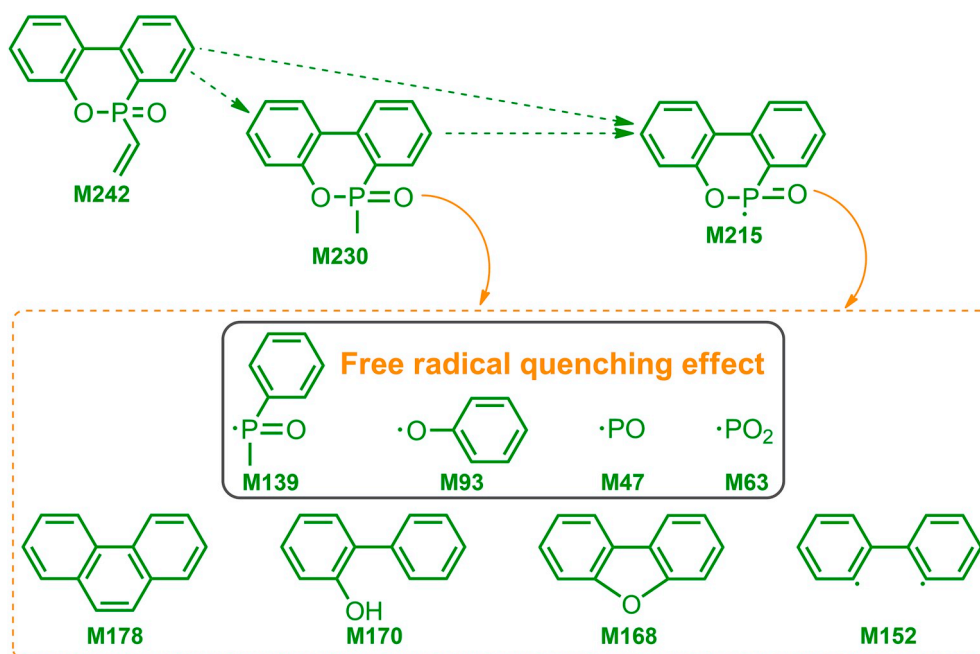


Fig. 11. Presumptive pyrolysis routes of phosphaphenanthrene-containing fragments.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.compositesb.2019.107481>.

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