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Study of the synergistic effect of polyhedral oligomeric octadiphenylsulfonylsilsesquioxane and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide on flame-retarded epoxy resins

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ABSTRACT

A novel flame retardant additive, polyhedral oligomeric octadiphenylsulfonylsilsesquioxane (ODPSS) has been used to retard combustion of an epoxy resin (EP) of DGEBA (di-glycidyl ether of bisphenol A) with curing agent 4,4′-diaminodiphenylsulphone (DDS). A series of flame-retarded EP was prepared with ODPSS and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) loaded. The flame retardant properties of the EP composites were characterized by the LOI, UL-94 and cone calorimeter test. The EP loading with 2.5 wt.% ODPSS/2.5 wt.% DOPO showed a longer TTI, lower value of p-HRR and higher flammability rating than that loading with 5 wt.% DOPO. The char residues of these EP composites after the cone calorimeter tests were investigated by FTIR and XPS. The thermal stability and pyrolytic gases of the EP composites were detected by TGA-FTIR and DSC. The results indicated that the mixture of ODPSS and DOPO had a remarkable synergistic effect on retarding flame of the EP composites.

1. Introduction

Epoxy resins with low shrinkage, superior solvent and chemical resistance, good mechanical and electrical properties, good dimensional stability and adhesive strength are widely used in the fields of coating, transportation, electronic and electrical industrials [1–3]. For meeting some application requirements, several approaches have been utilized to enhance the thermal properties and reduce flammability of epoxy resins [4–7]. Although halogen-containing-compounds have been widely used as co-monomers or additives with epoxy resins to obtain flame retardant materials, they have obvious disadvantages: they can release corrosive and super-toxic chemicals like halogenated dibenzodioxins and dibenzofurans on combustion [8,9]. Therefore, there is a trend to develop and apply the halogen-free flame retardants.

Epoxy resins modified by phosphorus-containing-compounds are more environmentally friendly and widely used. DOPO and its derivatives, which have high thermal stability, good oxidation resistance and good water resistance have received considerable attention due to their high reactivity [10–14]. Without co-additive, epoxy resins prepared with DOPO could not show high flame-retardant efficiency and good thermal stability of the resulted epoxy resins [15]. Therefore, organic phosphorus-based flame retardants with especially high efficiency are attractive and required. On the other hand, a major disadvantage of reactive-type additive is reduction in mechanical properties by reducing the crosslink density of epoxy resins. An interesting approach is using flame retardants exhibiting the phosphorus–silicon synergism of flame retardancy [16–18]. The drawbacks of poor compatibility, migration, and leaching, which usually accompany traditional additive-type flame retardants, were reduced by the formation of the silica network [19]. It is worth to be mentioned that Zhang and co-workers detected an interesting phenomenon, termed the "blowing-out extinguishing effect", in flame-retarded epoxy resins loaded with DOPO-POSS which contains phosphorus and silicon [20,21].

Polyhedral oligomeric silsesquioxanes (POSSs) are structurally well-defined caged molecule with the general formula $(RSiO_{1.5})_n$ (where n is commonly 6, 8, or 10). The incorporation of POSS in polymers modifies both the thermal stability and the mechanical properties of matrix [22–32]. In our previous work, we synthesized a novel polyhedral oligomeric octadiphenylsulfonylsilsesquioxane via Friedel–Crafts reaction [33]. We also proved its characteristic of superior thermal stability in both air and nitrogen. The

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incorporation of ODPSS at a low loading content not only improved the glass-transition temperature of the EP composites but also enhanced their tensile strength. This work presents a study of the design and preparation of a synergistic flame-retardant system for epoxy resins that overcomes many of the aforementioned drawbacks. Furthermore, in order to verify the blowing-out effect, ODPSS, DOPO and a mixture of them have been used as flame retardants for epoxy resins. Flame retardancy and thermal degradation mechanism of epoxy resin composites based on the ODPSS and DOPO have been studied.

2. Experimental

2.1. Materials

Di-glycidyl ether of bisphenol A (DGEBA, E-44, epoxy equivalent 0.44 mol/100 g) was purchased from FeiCheng DeYuan Chemicals Co., ltd. 4,4′-diaminodiphenylsulphone (DDS) was purchased from TianJin GuangFu Fine Chemical Research Institute.9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (Scheme 1) was purchased from Eutec Trading (Shanghai) Co., Ltd. ODPSS (Scheme 1) was synthesized in our laboratory.

2.2. Preparation of the cured epoxy resins

The cured epoxy resins were obtained using a thermal curing process. At first, the flame retardants (DOPO, ODPSS, ODPSS/DOPO) were dispersed in DGEBA by mechanical stirring at 140 °C for 1 h. The contents of the flame retardants used in the EP composites are listed in Table 1. The mixture was always homogeneous and transparent liquid. After that, the curing agent DDS was added relative to the amount of DGEBA. The equivalent weight ratio of DGEBA to DDS was 100:27.3. The epoxy resins were cured at 180 °C for 4 h.

2.3. Measurements

The limiting oxygen index (LOI) was obtained using the standard GB/T 2406-93 procedure, which involves measuring the minimum oxygen concentration required to support candle-like combustion of plastics. An oxygen index instrument (Rheometric Scientific Ltd.) was used on samples of dimensions 100 × 6.5 × 3 mm^3. Vertical burning tests were performed using the UL-94 standard on samples of dimensions 125 × 12.5 × 3.2 mm^3. In this test, the burning grade of a material was classified as V-0, V-1, V-2 or no rating (NR), depending on its behavior (dripping and burning time).

Thermal gravimetric analysis (TGA) was performed with a Netzsch 209 F1 thermal analyzer, with the measurements carried out in a nitrogen atmosphere at a heating rate of 20 °C/min from 40 °C to 800 °C. 5 mg samples were used for each measurement, with a gas flow rate of 60 ml/min. The typical results from TGA were reproducible within ±1%, and the reported data were averages of three measurements. To detect the gas species given off, the TGA was coupled with a Fourier transform infrared spectrometer (TGA-FTIR, Nicolet 6700). The connection between the TGA and FTIR was effected with a quartz capillary held at a temperature of 200 °C.

Differential scanning calorimetry (DSC) curves of the EP composites were measured using a Netzsch 204 F1 differential scanning calorimeter with a pressure cell. Samples (5–10 mg) were tested at a heating rate of 10 °C/min and results from the second heating in the range 30–250 °C are reported. Typical results from DSC were reproducible within ±1%, and the reported results are the average of three measurements.

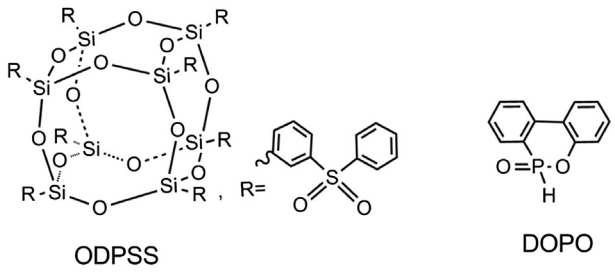
Cone calorimeter measurements were performed according to ISO 5660 protocol at an incident radiant flux of 50 kW/m^2. The equipment is Fire Testing Technology apparatus with a truncated cone-shaped radiator. The specimen (100 × 100 × 3 mm^3) was measured horizontally without any grids. Typical results from the cone calorimeter tests were reproducible within ±10%, and the reported parameters were the averages of three measurements.

To investigate the condensed phase of the EP composites, all the cone calorimeter tests were stopped at 600 s. The residues were cooled under room conditions. Samples of the exterior chars (5 mm thickness) were ground and analyzed by FTIR (Nicolet 6700) in ATR mode.

The X-ray photoelectron spectroscopy (XPS) data were obtained using a Perkin–Elmer PHI 5300 ESCA system at 250 W (12.5 kV at 20 mA) under a vacuum better than 10^{-6} Pa (10^{-8} Torr). The char residues were the same as those used in the FTIR. Typical results from the XPS were reproducible within ±3%.

Table 1
Compositions of flame-retarded EP composites.

Samples	Cured EP (wt.%)	ODPSS content (wt.%)	DOPO content (wt.%)	P Content (wt.%)	Si content (wt.%)
EP-control	100.0	0.00	0.00	0.00	0.00
EP-1	95.0	5.00	0.00	0.00	0.52
EP-2	95.0	0.00	5.00	0.72	0.00
EP-3	95.0	3.75	1.25	0.18	0.39
EP-4	95.0	2.50	2.50	0.36	0.26
EP-5	95.0	1.25	3.75	0.54	0.13



Scheme 1. Chemical structures of ODPSS and DOPO molecules.

3. Results and discussion

3.1. Flame retardancy of the cured EP composites

3.1.1. LOI analysis

The effects of flame retardants (ODPSS, DOPO, ODPSS/DOPO) on the LOI values of the epoxy resins are presented in Table 2. We observed that the increase of LOI value for the epoxy resins was limited with only ODPSS added. However, the LOI values of 5 wt.% of the mixture of ODPSS and DOPO systems increased remarkably throughout with increasing the DOPO content. Moreover, when only DOPO was incorporated, the LOI value was leveled up to 33.7%

Table 2
Flame retardancy of EP/ODPSS/DOPO composites.

Samples	P Content (wt.%)	LOI (%)	UL-94 (3.2 mm)	t_1 (s)	t_2 (s)	Dripping
EP-control	0.00	23.2	NR	>60	/	Yes
EP-1	0.00	24.3	NR	>60	/	No
EP-2	0.72	33.7	V-1	8	10	No
EP-3	0.18	28.0	V-1	16	8	No
EP-4	0.36	29.8	V-0	4	3	No
EP-5	0.54	30.9	V-0	3	3	No