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Blowing-out effect in epoxy composites flame retarded by DOPO-POSS and its correlation with amide curing agents

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ABSTRACT

A novel polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) has been used to flame retard DGEBA (diglycidyl ether of bisphenol A) epoxy resins cured by two amides, namely the aliphatic oligomeric polyamide 650 (PA650) and the aromatic 4,4′-diaminodiphenylsulphone (DDS). The epoxy composites with DOPO-POSS showed different flame retardant properties depending on the amide used. The results of UL-94 tests show that the DEGBA/DDS with DOPO-POSS exhibits a blowing-out effect through vigorous emission of pyrolytic gases, but the DEGBA/PA650 does not. Moreover, only 2.5 wt.% DOPO-POSS imparts to the epoxy resin DEGBA/DDS a LOI value of 27.1% and UL-94 V-1 rating. In contrast, 10 wt.% DOPO-POSS in the DEGBA/PA650 results in a LOI value of 25.9% and a UL-94 V-1 rating. The details of fire behaviour, such as the values of TTI, HRR, p-HRR, COPR, and CO_2PR have been tested using a cone calorimeter. DOPO-POSS in the DEGBA/DDS causes a lower value of p-HRR and longer TTI than in the DEGBA/PA650. The DEGBA/DDS with even as little as 2.5 wt.% DOPO-POSS easily forms a compact char. However, the DEGBA/PA650 with DOPO-POSS does not char until 10 wt.% DOPO-POSS has been added. The thermal stability and pyrolytic gases of the two kinds of epoxy resins were assessed by TGA-FTIR under a nitrogen atmosphere. DOPO-POSS performs better in accelerating charring in the DDS curing system compared with the PA650 curing system. It is postulated that for the DEGBA/DDS/DOPO-POSS, fast and dense charring and accumulating of pyrolytic gases in the char contribute to the blowing-out effect. By contrast, the aliphatic chain of the PA650 is easy to break down and produce combustible gases, so does not easily form a crosslinked structure in the condensed phase until enough DOPO-POSS has been added. These results may be very helpful for investigation of the conditions under which the blowing-out effect in epoxy resins can be caused by synergy of phosphorous (DOPO) and silicon (POSS).

1. Introduction

Epoxy resin (EP) has become a very important thermosetting material because of its excellent mechanical and chemical properties. It is used as a high-performance material in many fields, such as an adhesive, coating, laminating capsulation, electronic/electrical insulation, and for composite applications. However, the fire risk remains a major drawback of these materials [1–4]. Halogen-containing flame retardants are reported to be effective flame retardants for epoxy resins. However, some of these are restricted in their use because they generate dense toxic smoke and corrosive products during combustion [5]. Therefore, the preparation and application of halogen-free flame retardants has been the subject of extensive investigation.

Organic–inorganic hybrid composites are normally considered to be a new generation of high-performance materials, as they combine the advantages of inorganic materials with those of organic polymers [6,7]. Polyhedral oligomeric silsesquioxanes (POSS) have the chemical composition ($RSiO_{1.5}$), where R is hydrogen or any alkyl, alkylene, aryl, or arylene group, or a number of other organo-functional derivatives, and is similar in composition to both silica (SiO_2) and silicone (R_2SiO) [8,9]. POSS molecules, with a nanosized, cage-shaped, three-dimensional structure, can be incorporated into almost any type of thermoplastic or thermosetting polymer to improve their thermal properties and oxidation resistance and flame retardancy [10,11].

Phosphorous compounds can impart flame retardancy through flame inhibition in the gas phase and the condensed phase [12,13]. Several non-reactive and reactive phosphorus-containing flame

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retardants for epoxy resins have been investigated in recently published work [14–16]. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a cyclic phosphate with a diphenyl structure which has high thermal stability, and good resistance to oxidation and water [17,18]. Using DOPO or its derivatives as flame retardants, significant improvements in the fire behaviour of epoxy resins have been reported [14–16].

In our previous work, the DOPO-containing polyhedral oligomeric silsesquioxane (DOPO-POSS) (Scheme 1) was synthesized successfully [19]. In addition, an interesting phenomenon, called the "blowing-out effect", has been detected in flame retarded epoxy resins loaded with DOPO-POSS. The model of the blowing-out effect is shown in Scheme 2 [20,21]. In order to further understand the reasons behind and the factors that influence the blowing-out effect, we have examined the use of DOPO-POSS as a flame retardant for epoxy resins cured by both oligomeric polyamide 650 (PA650) and 4,4′-diaminodiphenylsulphone (DDS) (Scheme 3). This work presents a study of the responses of flame retarded EP composites following exposure to fire.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, E-44, epoxy equivalent = 0.44 mol/100 g) was purchased from FeiCheng DeYuan Chemicals CO., LTD. The oligomeric polyamide 650 (PA650) and 4,4′-diaminodiphenylsulphone (DDS) were purchased from TianJin GuangFu Fine Chemical Research Institute. DOPO-POSS was synthesized in our laboratory. DOPO-POSS was mixture of perfect T_8 cage and imperfect T_9 cage with one Si–OH group on it [19].

2.2. Preparation of the cured epoxy resins

The cured epoxy resins were obtained using a thermal curing process. At first, the DOPO-POSS was dispersed in DGEBA by mechanical stirring at 140 °C for 1 h and it would dissolve in DGEBA. The mixture is homogeneous and transparent liquid always. After that, the curing agent DDS was then added relative to the amount of DGEBA. The equivalent weight ratio of DGEBA to DDS was 20:9. The epoxy resins were cured at 180 °C for 4 h. For the PA650, the mixture cooling to 40 °C, the curing agent then added relative to the amount of DGEBA. The equivalent weight ratio of DGEBA to PA650 was 2:1. The epoxy resins were cured at 80 °C for 4 h. The LOI and UL-94 test samples were strips. The contents of the DOPO-POSS in the EP composites are listed in Tables 1 and 2.

2.3. Measurements

The limiting oxygen index (LOI) was obtained using the standard GB/T2406–93 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 unclassified, depending on its behaviour (dripping and burning time).

Thermal gravimetric analysis (TGA) was performed with a Netzsch 209 F1 thermal analyser, with the measurements carried out in a nitrogen atmosphere at a heating rate of 20 °C/min from 40 °C to 800 °C. 10 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 are 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.

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 are the average of three measurements.

To investigate the condensed phase of the EP composites, all the cone calorimeter tests were stopped at 500 s. The residue was cooled under room conditions. A sample of the exterior char of about 1 cm thickness was ground and analysed by FTIR (Nicolet 6700) in ATR mode.

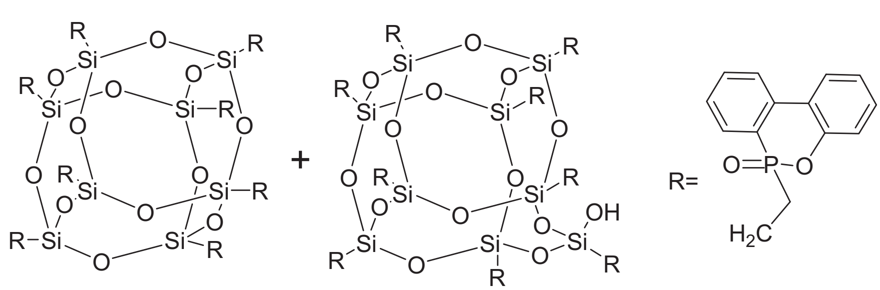
3. Results and discussion

3.1. Flame retardancy of the cured epoxy resins

In order to understand the connection between the presence of DOPO-POSS and the blowing-out effect, the flame retardancy of epoxy resins (EP) cured using both oligomeric aliphatic PA650 and aromatic DDS curing agents has been investigated by way of the LOI and UL-94 tests.

The UL-94 test results of the DGEBA/DDS composites are shown in Table 1. It is clear that the flame retardancy of the epoxy resins is enhanced by loading with DOPO-POSS. No dripping is observed for any of the samples and self-extinguishing is observed with samples loaded with 2.5 and 5.0 wt.% DOPO-POSS. It is important to point out that the extinguishing is caused by the blowing-out effect [20] but this effect is weakened with increase of the DOPO-POSS content.

In the case of the DGEBA/PA650 composites, as shown in Table 2, enhanced flame retardancy appears with the increase of DOPO-POSS loading. The dripping phenomenon is no longer observed and self-extinguishing takes place with 10 wt.% DOPO-POSS



Scheme 1. Typical chemical structures of DOPO-POSS molecules.