



Comparison of intumescence mechanism and blowing-out effect in flame-retarded epoxy resins



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ABSTRACT

Epoxy resins (EPs) have been flame-retarded by an APP–MMT nanocomposite (ammonium polyphosphate montmorillonite nanocomposite) and an OPS/DOPO (octaphenyl polyhedral oligomeric silsesquioxane/9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) mixture, respectively. The flame retardancies and efficiencies of these systems have been investigated by LOI, UL-94, and cone tests. The OPS/DOPO mixture (blowing-out effect) was found to be more efficient for improving LOI, UL-94, p-HRR, and THR. However, 10 wt.% of the APP–MMT nanocomposite (intumescence mechanism) showed good flame retardancy and higher efficiency in reducing TSR. The flame retardancy mechanisms of the APP–MMT nanocomposite and the OPS/DOPO mixture have been investigated by TGA–FTIR, PY–GC/MS, FTIR, and SEM analyses. The results indicate that the APP–MMT nanocomposite accelerated the decomposition of epoxy resins, with most of the pyrolytic products consisting of small molecules. Furthermore, the melt viscosities of the pyrolytic residues correspond to the rate of gas release, which allows the formation of an intumescent and firm char layer. The OPS/DOPO mixture caused the epoxy resin to decompose rapidly, giving complex pyrolytic products. Moreover, EP/OPS/DOPO rapidly produced $-\text{Si}-\text{O}-\text{C}-$ or $-\text{Si}-\text{O}-\text{P}(=\text{O})-\text{C}-$ cross-linked structures in the condensed phase under the action of heat, leading to formation of solid carbonaceous char. Because EP/OPS/DOPO decomposed rapidly, the hard char layer could not swell to accommodate the released gases, and consequently blowing-out could occur. The differences between intumescence and the blowing-out effect are caused by differences in the structures of the char layers and the rates of gas emission.

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1. Introduction

Epoxy resins (EP) are very important thermosetting materials owing to their excellent mechanical and chemical properties [1–3]. They are widely applied in advanced composite matrices in the electronic/electrical industries, for which a highly flame-retardant grade is required. The fire risk remains a major drawback of these materials [4]. Halogen-containing compounds are effective flame retardants for epoxy resins. Their effect relies on the pyrolysis products of halogen-based flame retardants producing X^{\bullet} (Cl^{\bullet} or Br^{\bullet}) radicals and HX , which could scavenge the polymer degradation radicals (H^{\bullet} and $\bullet\text{OH}$) in the gas phase, leading to an inhibition of flame propagation [5]. However, due to environmental concerns, some halogen-containing flame retardants have been gradually prohibited [6,7].

Phosphorus-containing compounds are important flame retardants for epoxy resins. They impart flame retardancy through flame inhibition in the gas phase and char enhancement in the condensed phase [8–10]. For example, ammonium polyphosphate (APP) is very effective for the flame retardation of epoxy resins [11]. Its principal flame-retardancy mechanism is that of “intumescence”, whereby flame retardants swell, bubble, and char on exposure to a flame and the carbonaceous porous foamed mass acts as a barrier to heat, air (O_2), and pyrolysis products. This is a typical condensed-phase flame-retardancy mechanism. However, the intumescent char layer cannot be created without the cooperation of appropriate gas release. Furthermore, the gas in the bubbles could retard heat transfer more effectively than a solid char layer [12–14].

Recently, our group reported a novel flame-quenching mechanism termed the “blowing-out effect”, which was found in epoxy resins flame retarded by DOPO-POSS, that depends on synergy between the gas phase and the condensed phase [15,16]. The

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“blowing-out effect” has been described as follows: “after the sample was ignited, it showed an unstable flame for several seconds; with the pyrolytic gaseous products jetting outward from the condensed-phase surface, the flame was extinguished, it looked like the gas blew out the flame”.

The intumescence mechanism and the blowing-out effect both depend on the synergy between the gas phase and condensed phase. In this research, epoxy resins (EPs) have been flame retarded by an APP–MMT nanocomposite and an OPS/DOPO mixture, allowing detailed comparison of the intumescence mechanism and the blowing-out effect. The respective combustion phenomena, extinction processes, gas-phase species, and condensed-phase structures have been investigated.

2. Experimental

2.1. Materials

Diglycidyl ether of biphenol A (DGEBA, E-44, epoxy equivalent = 0.44 mol/100 g) was purchased from FeiCheng DeYuan Chemicals CO., LTD. The 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. Octaphenyl polyhedral oligomeric silsesquioxane (OPS) (Scheme 1) was synthesized in our laboratory with perfect T_8 cage [17]. Ammonium polyphosphate montmorillonite nanocomposite (APP–MMT nanocomposite) (Scheme 1) was prepared in our laboratory, which contain 6wt.% NaMMT [18].

2.2. Preparation of the cured epoxy resins

The cured epoxy resins were obtained using a thermal curing process. At first, the flame retardants were dispersed in DGEBA by mechanical stirring at 140 °C for 1 h and it would disperse in DGEBA. The mixture is homogeneous 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 9:2. The epoxy resins were cured at 180 °C for 4 h. The LOI and UL-94 test samples were strips. The contents of the flame retardant in the EP composites are listed in Table 1.

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 $100 \times 6.5 \times 3 \text{ mm}^3$. Vertical burning tests were performed using the UL-94 standard on samples of dimensions $125 \times 12.5 \times 3.2 \text{ mm}^3$. In this test, the burning grade

Table 1
Composition of the investigated materials (wt.%).

Samples	Cured epoxy resins	APP–MMT	OPS	DOPO	P content	Si content
Pure EP	100.0	/	/	/	/	/
EP/APP–MMT	94.8	10.0	/	/	≈ 3.3	/
EP/OPS/DOPO	94.8	/	2.5	2.5	0.54	0.36

of a material was classified as V-0, V-1, V-2 or unclassified, depending on its behavior (dripping and burning time).

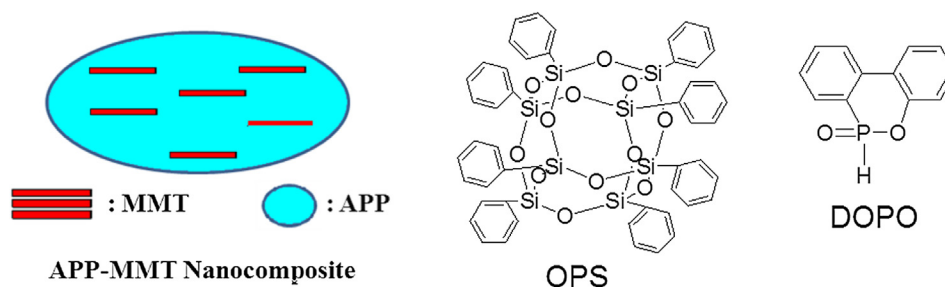
Cone calorimeter measurements were performed according to ISO 5660 protocol at an incident radiant flux of 50 kW/m^2 . The equipment is Fire Testing Technology apparatus with a truncated cone-shaped radiator. The specimen ($100 \times 100 \times 3 \text{ mm}^3$) was measured horizontally without any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

To investigate the flame retardancy efficiency of APP–MMT and OPS/DOPO, some calculations have been adopted. For the LOI, TTI, p-HRR, THR and TSR, the changes of their values (flame retarded EP composites minus pure EP) are divided by the content of flame retardants or flame retardant elements. Furthermore, the influence of matrix content changes has been considered for the calculated function of the p-HRR, THR and TSR.

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 . 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 $\pm 1\%$, 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 .

Pyrolysis/gas-chromatograph/mass spectrometer (PY–GC/MS) analysis were performed using a vertical micro-furnace type double-shot pyrolyzer PY2020iD (Frontier Laboratories Ltd., Fukushima, Japan) attached to a GC/MS system (Agilent 6890). The evolved gases from pyrolysis were transferred on line to a gas chromatograph by using a capillary transfer line. The gas chromatograph was equipped with a low to-mid polarity-fused silica capillary column (J&W Scientific) of $30 \text{ m} \times 250 \mu\text{m} \times 0.25 \mu\text{m}$ film thickness. The oven temperature was held at 80 °C for 3 min and then increased to 850 °C at 10 °C/min in the scan modus. The carrier gas was helium at a controlled flow of 1 ml/min . The detector consisted of an Agilent 5973 mass selective detector and electron impact mass spectra were acquired with 70 eV ionizing energy.

To investigate the condensed phase of the EP composites, all the cone calorimeter tests were stopped at 500 s. The residue was



Scheme 1. Typical chemical structures of OPS, DOPO and APP–MMT nanocomposite.

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