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Pyrolysis and fire behaviour of epoxy resin composites based on a phosphorus-containing polyhedral oligomeric silsesquioxane (DOPO-POSS)

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ABSTRACT

The pyrolysis and fire behaviour of epoxy resin (EP) composites based on a novel polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) and diglycidyl ether of bisphenol A (DGEBA) have been investigated. The pre-reaction between the hydroxyl groups of DOPO-POSS and the epoxy groups of DGEBA at 140 °C is confirmed by FTIR, which means that DOPO-POSS molecules of hydroxyl group could easily disperse into the epoxy resin at the molecular level. The EP composites with the DOPO-POSS were prepared through a curing agent, m-phenylenediamine (m-PDA). The morphologies of the EP composites observed by SEM indicate that DOPO-POSS disperses with nano-scale particles in the EP networks, which implies good compatibility between them. The thermal properties and pyrolysis of the EP composites were analyzed by DSC and TGA, TGA-FTIR, and TGA–MS. The analysis indicates that the DOPO-POSS change the decomposition pathways of the epoxy resin and increase its residue at high temperature; moreover, the release of phosphorous products in the gas phase and the existence of Si–O and P–O structures in the residue Is noted. The fire behaviour of the EP composites was evaluated by cone calorimeter (CONE). The CONE tests show that incorporation of DOPO-POSS into epoxy resin can significantly improve the flame retardancy of EP composites. SEM and XPS were used to explore micro-structures and chemical components of the char from CONE tests of the EP composites, they support the view that DOPO-POSS makes the char strong with the involvement of Si–O and P–O structures.

1. Introduction

Epoxy resins are very important thermosetting materials owing to their excellent mechanical and chemical properties [1–3]. They are widely applied as advanced composite matrices in electronic/electrical industries where a remarkable flame-retardant grade is required, but the fire risk is a major drawback of these materials [4]. Recently the research efforts on epoxy resins have been focused on improving their thermal stability, increasing glass transition temperatures and enhancing flame retardancy [1,5–7]. Traditionally, halogenated compounds are widely used as co-monomers or additive with epoxy resins to obtain fire-retardant materials. However, flame-retardant epoxy resins containing bromine or chlorine can produce poisonous and corrosive smoke and may give super toxic halogenated dibenzodioxins and dibenzofurans [4]. Because of environmental concerns, some halogen-containing flame retardants that have high flame-resistant efficiencies have been gradually prohibited [8,9].

Organic–inorganic hybrid composites are typically considered a new generation of high-performance materials, as they combine the advantages of inorganic materials with those of organic polymers [10–13]. Polyhedral oligomeric silsesquioxanes (POSS) have the chemical composition ($RSiO_{1.5}$), where R is hydrogen or any alkyl, alkylene, aryl, or arylene group, or organo-functional derivatives thereof, similar to the compositions of both silica (SiO_2) and silicone (R_2SiO) [14,15]. POSS molecules with a nanosized, cage-shaped, three-dimensional structure can be incorporated into almost all kinds of thermoplastic or thermosetting polymers to improve their thermal properties and oxidation resistance and flame retardancy [16–19].

Phosphorous compounds could impart flame retardancy through flame inhibition in the gas phase and char enhancement in the condensed phase [4,20–22]. Several either nonreactive or reactive phosphorus-containing flame retardants in epoxy resins have been investigated in recent research articles [23–26]. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is

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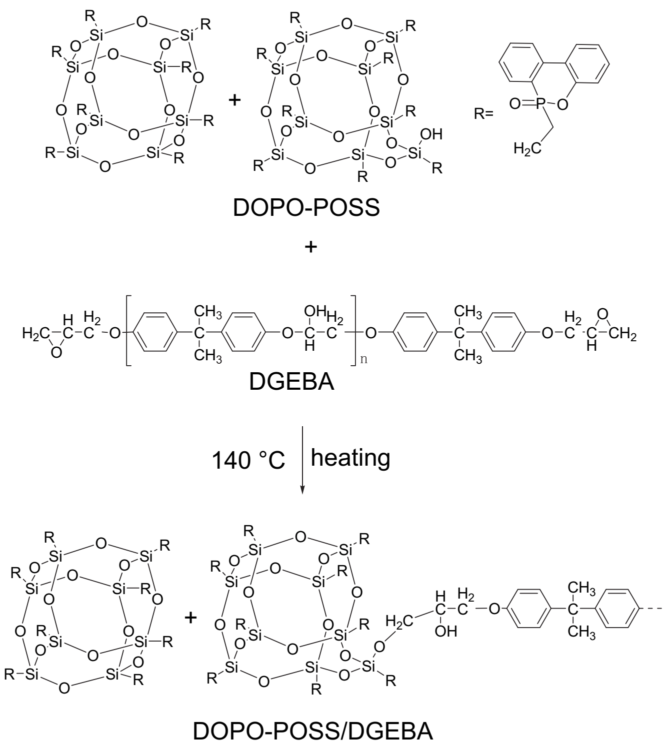


Scheme 1. Reaction process between DOPO-POSS and DGEBA.

a cyclic phosphate with a diphenyl structure, which has high thermal stability, good oxidation and water resistance [27–30]. Using DOPO or its derivatives as flame retardant, significant improvement in the fire behaviour of epoxy resins has been reported [23–26].

In our previous work [31,32], we described the successful synthesis of DOPO-containing polyhedral oligomeric silsesquioxane (DOPO-POSS) (Scheme 1). It is a novel phosphorus-containing POSS with high thermal stability, which may be an efficient halogen-free flame-retardant system for epoxy resin. In this article, flame retardancy and thermal degradation mechanism of epoxy resin composites based on the DOPO-POSS have been studied.

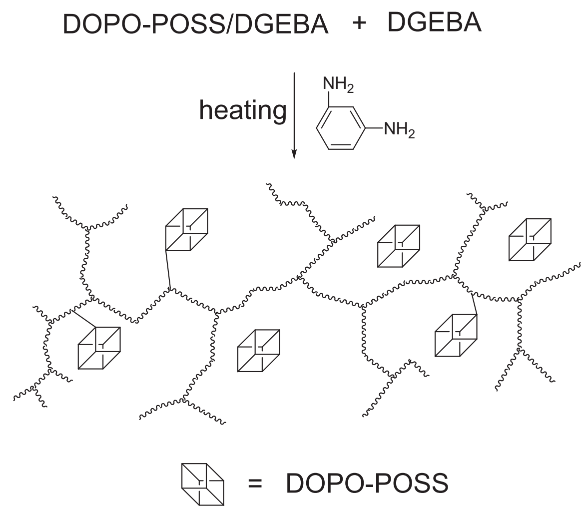
2. Experimental

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. m-Phenylenediamine (m-PDA) was purchased from TianJin GuangFu Fine Chemical Research Institute. DOPO-POSS was synthesized in our laboratory [31,32]. DOPO-POSS was mixture of perfect T_8 cage and imperfect T_9 cage with one Si—OH group on it.

Table 1
Compositions of EP/DOPO-POSS composites.

Materials	EP control	EP-1	EP-2	EP-3
DGEBA (g)	100.0	100.0	100.0	100.0
m-Phenylenediamine (g)	12.0	12.0	12.0	12.0
DOPO-POSS (g)	0	5.89	12.44	28.00
DOPO-POSS (wt%)	0	5	10	20



Scheme 2. Preparation of EP composites.

2.2. Synthesis of DOPO-POSS/DGEBA

The Si—OH group in DOPO-POSS is expected to react with the epoxide group in the DGEBA. The pre-reaction between DOPO-POSS and epoxy resin may enhance the compatibility of them. First, 28 g of DOPO-POSS and 100 g DGEBA were mixed in a three-necked flask. The temperature of the reaction mixture was raised to 140 °C and held at that temperature for 2 h. After that, the mixture was added into ethyl acetate. The resulting DOPO-POSS/DGEBA was obtained as a white powder after suction filtration. The synthesis process is illustrated in Scheme 1.

2.3. Preparation of EP composites

To realize pre-reaction between DOPO-POSS and epoxy resin, all of the DOPO-POSS was dispersed in DGEBA at 140 °C for 2 h before the curing. The contents of the DOPO-POSS in the EP composites were adjusted to be 5, 10, and 20 wt.%. After the system cooling to 70 °C, the curing agent (m-PDA) was then added. The equivalent weight ratio of DGEBA to m-PDA was 25:3, which are listed in Table 1. The mixtures were cured at 80 °C for 2 h and post-cured at

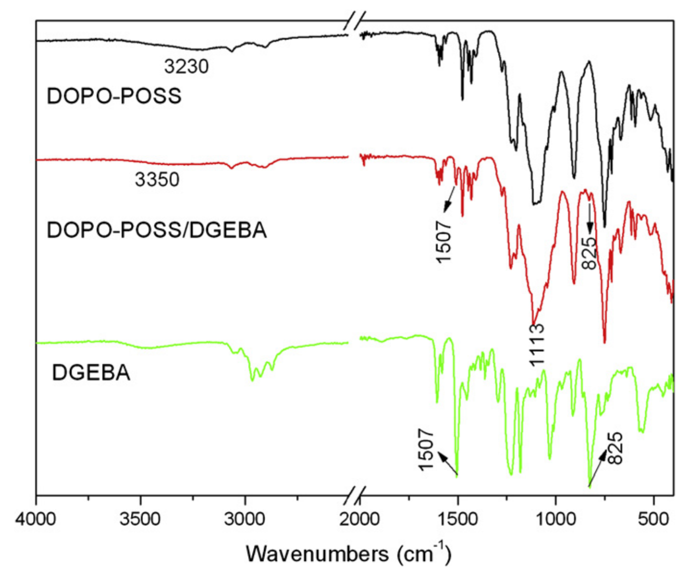


Fig. 1. FTIR spectra of DOPO-POSS, DGEBA, and DOPO-POSS/DGEBA.