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Investigations of epoxy resins flame-retarded by phenyl silsesquioxanes of cage and ladder structures

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ABSTRACT

Cage-type octaphenyl silsesquioxane (OPS) and ladder-type polyphenyl silsesquioxane (PPSQ) have been used as flame-retardants in epoxy resins (EPs) in the presence and absence of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). The flame retardancy of these EPs have been tested by the LOI and UL-94 standard tests, and details of fire behaviors, such as TTI, HRR, p-HRR, THR, COPR, and CO_2PR, have been tested using a cone calorimeter. The results have shown that OPS has distinctly different effects on the flame retardancy of EPs compared to those of PPSQ. In the UL-94 test, the flame-retarded EP with OPS showed a weak blowing-out effect, but the flame-retarded EP with PPSQ did not; further, the flame-retarded EP with DOPO/OPS showed a significant blowing-out effect, but the flame-retarded EP with DOPO/PPSQ did not. According to the cone tests, addition of PPSQ to EPs, with or without DOPO, causes higher p-HRR; on the contrary, the addition of OPS to EPs leads to lower p-HRR compared to that of the neat EP. The thermal stability of these EPs has been investigated by TGA. The morphology of the chars after the cone tests has been investigated by visual observation, SEM, and XPS. Observation of the chars suggested that OPS can assist the EP, especially the EP with DOPO, to form stronger and denser chars than PPSQ, although PPSQ with a ladder structure has higher thermal stability than that of cage-type OPS. It was also observed that the Si concentration in the interior chars from the EPs with PPSQ was higher than that in those from the EPs with OPS. It is supposed that in the composites of EP or EP/DOPO, slow charring of PPSQ cannot match the intumescent and charring process of the EPs during combustion, but OPS can. This may explain why OPS exhibits significantly different flame retardancy on the EPs compared to PPSQ.

1. Introduction

Epoxy resins are commonly used as advanced composite matrices in the electronic and electrical industries, where a high-quality flame-retardant grade is required because the fire risk is a major drawback of these materials [1–5]. Traditionally, halogenated compounds have been widely used as co-monomers or additives 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 produce highly toxic halogenated dibenzodioxins and dibenzofurans [6–8]. Therefore, the development and application of halogen-free flame-retardants has been a subject of extensive investigation in relation to epoxy resins.

Silsesquioxanes are typical organic–inorganic hybrid composites, and are widely considered to be a new generation of high-performance materials [9–12]. Silsesquioxanes can be incorporated into almost any kind of thermoplastic or thermosetting polymer to improve their mechanical and thermal properties and oxidation resistance, and to reduce their flammability [13,14]. In recent years, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have received outstanding attention because of their high reactivity and applicability on flame retardancy [15–19]. Using DOPO or its derivatives as flame retardant for epoxy resins have been reported [20–25].

In our previous work, a DOPO-containing polyhedral oligomeric silsesquioxane (DOPO-POSS) was successfully synthesized [26]. An interesting phenomenon, termed the "blowing-out effect", has been detected in flame-retarded epoxy resins with DOPO-POSS loading [27]. Moreover, the "blowing-out effect" can also be created in epoxy resins flame-retarded by a mixture of OPS (octaphenyl silsesquioxane) and DOPO [28]. The "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

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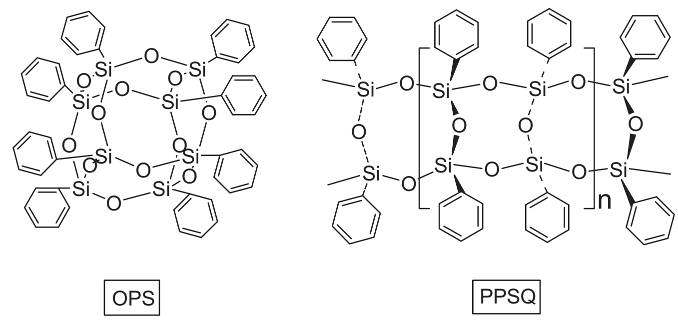
surface, the flame was extinguished; it looks as though the gas blew out the flame". A model of the blowing-out effect is shown in Fig. 1. This concept reveals that the blowing-out effect is simultaneously determined by the rate of production of gases and the properties of the condensed char [29].

In this study, in order to further understand the "blowing-out effect", cage-type OPS (octaphenyl silsesquioxane) and ladder-type PPSQ (polyphenyl silsesquioxane), respectively, have been incorporated into pure EP or EP/DOPO composites to enhance their flame retardancy. The influences of phenyl silsesquioxanes of cage or ladder structures on the flame retardancy and blowing-out effect of epoxy resin are reported in detail.



Scheme 1. Typical chemical structures of OPS and PPSQ.

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. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Eutec Trading (Shanghai) Co., Ltd.

2.2. Synthesis of the silsesquioxanes

Two kinds of silsesquioxanes are shown in Scheme 1. Octaphenyl silsesquioxane (OPS) was synthesized by the hydrolysis and condensation of phenyltrichlorosilane according to a previously reported procedure [30]. The OPS obtained in this way had a perfect T_8 cage structure. Polyphenyl silsesquioxane (PPSQ) was synthesized by the hydrolysis and condensation of phenyltrichlorosilane using a special catalyst under certain conditions. XRD and ^{29}Si NMR results indicated that the PPSQ was a ladder-type polymer [31].

2.3. Preparation of the EP composites

To prepare the pure EP and EP/silsesquioxane systems, OPS or PPSQ was dispersed in DGEBA by mechanical stirring at 140 °C for 1 h. After cooling the EP mixture to 80 °C, the curing agent *m*-PDA was added. The molar ratio of amino group to epoxy group is controlled at 1:1, correspondingly, the amounts of m-PDA and DGEBA are 12 g and 100 g, respectively. The liquid mixtures were poured into a mold, cured at 80 °C for 2 h, and post-cured at 150 °C for 2 h.

To prepare the EP/DOPO and EP/DOPO/silsesquioxane systems, DOPO was added to DGEBA by mechanical stirring at 140 °C for 1 h, and then OPS or PPSQ was dispersed in the DGEBA/DOPO for a further 1 h. Thereafter, the same preparation processes as described above were followed.

The contents of OPS, PPSQ, and DOPO in the products are listed in Table 1. The samples were cut into strips to carry out the LOI and UL-94 tests.

2.4. 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 barrel-shaped samples of dimensions $100 \times 6.5 \times 3$ mm^3. Vertical burning tests were performed using the UL-94 standard on samples of dimensions $125 \times 12.5 \times 3.2$ mm^3. In this test, the burning grade of a material was classified as V-0, V-1, V-2 or NR (unclassified), depending on its behavior (dripping and afterflame time). The t1 (t2) is afterflame time after the first (second) ignition of sample.

Thermal gravimetric analysis (TGA) was performed with a Netzsch 209 F1 thermal analyzer, with the measurements carried

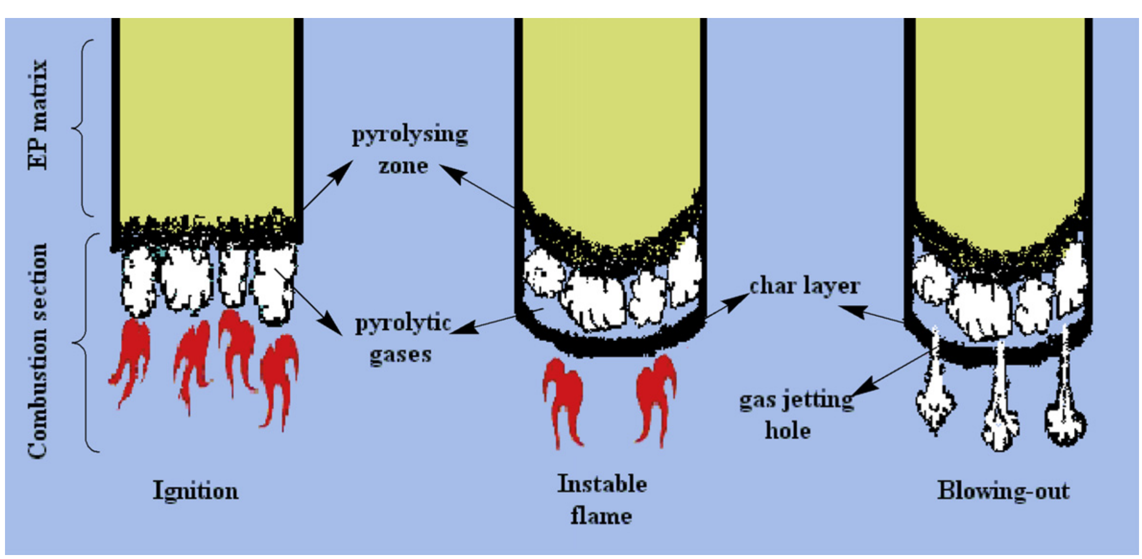


Fig. 1. Model of the blowing-out effect.