Polymer Degradation and Stability 131 (2016) 82–90

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Blowing-out effect in flame retarding epoxy resins: Insight by temperature measurements during forced combustion

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ARTICLE INFO

Article history:
Received 16 April 2016
Received in revised form
21 June 2016
Accepted 2 July 2016
Available online 2 July 2016

Keywords:
Epoxy resin
DOPO-POSS
Temperature measurement
Blowing-out effect
Cone calorimeter

ABSTRACT

The temperature measurements within burning epoxy resins (EPs) were used to study the thermo physical evolution up and inside of samples during different applied heat fluxes cone calorimeter tests. A series of flame retarded epoxy resins (EP) were prepared with polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS). The flame retardancy of these EPs was tested by both flammability tests (LOI, UL-94) and forced combustion in cone calorimeter, to assess DOPO-POSS effects on the flame retardancy of EP composites. 2.5 wt% DOPO-POSS incorporation into epoxy resin perform interesting blowing-out effect, which results in a LOI value 27.1 and UL-94 V-1 ($t_1 = 8$ s and $t_2 = 5$ s) rating. The details of fire behavior, such as the values of TTI, HRR, p-HRR, and THR have been tested using a cone calorimeter. The temperature measurements during cone calorimeter tests indicate that the char layer of EP/2.5 DOPO-POSS has the best performance on heat insulation and play an effective role (heat insulation) quicker than that of EP/5 DOPO-POSS or EP/10 DOPO-POSS. This heat insulation performance of char layer produced by EP/2.5 DOPO-POSS explains its good performance on LOI and UL-94 test.

1. Introduction

Epoxy resins are widely used as matrix materials for the fabrication of advanced composites in the electrical/electronic industry, owing to their high tensile strength and modulus, good adhesive properties, good chemical and corrosion resistance, low shrinkage on curing, and excellent dimensional stability [1–3]. However, as most of the organic polymers, flammability is one of the main drawbacks of the epoxy resins. In order to meet application requirements, their flame retardant properties have to been improved, while avoiding the use of environmentally impacting additives and maintaining other important characteristics such as mechanical and thermal properties [4–6]. Therefore, the preparation and application of halogen-free flame retardant is the subject of extensive investigation.

Phosphorus-containing compounds are important flame retardants for epoxy resins. These may impart flame retardancy through flame inhibition in the gas phase and/or char enhancement in the condensed phase [7–10]. Several non-reactive and reactive phosphorus-containing flame retardants for epoxy resins have been investigated in recently published work [11–14]. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a reactive phosphorus-containing flame retardant with a diphenyl structure which has high thermal stability, and good resistance to oxidation and water. Using DOPO or its derivatives as flame retardants, significant improvements in the fire behavior of epoxy resins have been reported [15–18].

Polyhedral oligomeric silsesquioxanes (POSS) are cage-like hybrid molecules, based on a core composed of silicon and oxygen, ranging in size from approximately 1 to 3 nm. 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 intermediate in the combination between silica (SiO_2) and silicone (R_2SiO) [19,20]. POSS molecules with a nanosized, cage-shaped, three-dimensional structure have been incorporated into almost all kinds of thermoplastic or thermosetting polymers by blending, grafting, cross-linking or copolymerization, in order to improve their mechanical and thermal properties and oxidation resistance, and to reduce their flammability [21–23].

An interesting phenomenon, which was tentatively named “blowing-out extinguishing effect”, has been detected in UL-94 test

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http://dx.doi.org/10.1016/j.polymdegradstab.2016.07.002
0141-3910/

for the epoxy resin with 2.5 wt% DOPO-POSS, which is a phosphorus-containing polyhedral oligomeric silsesquioxane [24]. The “blowing-out effect” is that: “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 looks like that the gas blew out the flame”. The blowing-out effect can be detected during UL94 flammability testing the DGEBA/DDS and DGEBA/m-PDA system which are flame retarded by DOPO-POSS [24,25]. The POSS/DOPO mixture also can make these epoxy resins perform blowing-out effect, but use POSS or DOPO alone cannot do the same [26,27]. Depend on the blowing-out effect, less than 0.9 wt% flame retardant elements (Si and P) resulted in dramatic reduction of epoxy resins flammability. However, replacing aromatic curing agent (DDS and m-PDA) by an aliphatic curing agent (oligomeric polyamide, PA650), the blowing-out effect was not observed [25]. The difference between fire reaction of DGEBA crosslinked with aromatic or aliphatic hardeners suggest a specificity of the blowing out effect, which may depend both on the gas composition and release rate, as well as on the physical properties of the condensed phase.

In order to get more insights into the physical properties of the condensed phase, temperature measurements within burning polymers can be used to study the mechanism of flame retardancy of polymer. Heating of a polymer sample during fire tests does not occur at a constant heating rate; indeed, after the initial heating stage, the endothermic pyrolysis of the polymer and the vaporization of decomposition products exert a temperature-levelling effects in the condensed phase of a burning polymer materials [28,29]. After the initial stage of combustion, incoming heat flux absorbed by the specimen no longer results in an increase in polymer temperature [29,30], but instead in a progressive consumption of material [31]. Schartel et al. used temperature measurements inside of bulk within burning polymer specimens to gain deeper experimental insight into the actual pyrolysis conditions and flame retardancy mechanism [32]. Fina et al. used temperature measurements to study the thermo physical evolution of the condensed phase of the neat polymer or polymer nanocomposites before ignition in cone calorimeter test, allowing to investigate the ignition behaviors of flammable polymer materials [33,34].

In our previous work, the temperature profile during UL-94 test and the properties of char formation of EP composites are investigated in detail and indicate that blowing-out effect has a gasbag under the char layer, which is effective to inhibit the heat transfer from the fire to the unburned polymer matrix [35]. Due to the additional heat flux, the EP composites didn’t show extinguishment caused by the blowing-out effect, but lots of gas jetting which like it happened in the UL-94 tests can be observed at the edge of the sample during cone calorimeter tests. So in order to get more insights into blowing-out effect, the temperature measurements within burning epoxy resins (EPs) are used to study the temperature evolution above and inside of samples during cone calorimeter tests performed at different applied heat fluxes. The details of the thermo physical evolution of EP composites were investigated and thoroughly described in this paper.

2. Experimental

2.1. Material

Diglycidyl ether of biphenol A (DGEBA, E-44, epoxy equivalent = 0.44 mol/100 g) was purchased from FeiChengDeYuan Chemicals CO., LTD. The 4, 4′-diaminodiphenylsulphone (DDS) was purchased from TianJinGuangFu 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 (Fig. 1) [36].

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 10: 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/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 behavior (dripping and burning time).

Cone calorimeter measurements were performed at an incident radiant flux of 50 kW/m^2, using Fire Testing Technology apparatus. 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.

Thermal gravimetric analysis (TGA) was performed with a PerkinElmer TGA 4000 thermal analyzer system, with the measurements carried out in a nitrogen or air atmosphere at a heating rate of 20 °C/min from 35 °C to 800 °C. 10 mg samples were used for each measurement, with a gas flow rate of 70 ml/min.

2.4. Temperature measurements during cone calorimeter tests

Cone calorimeter measurement for temperature measurements were performed at incident radiant flux of 35, 50, or 75 kW/m^2, using a Fire Testing Technology apparatus with a truncated cone-shaped radiator. The specimen (100 × 100 × 3 mm^3) was measured horizontally without any grids.

The temperature measurements were carried out during cone calorimeter tests, using three K-type 1 mm Inconel sheathed thermo-couples. The EP sample was drilled three holes with 1 mm diameter as shown in Fig. 2. Two holes were through the samples and one hole was a depth of 1.5 mm which is half of the thickness of the samples. The three holes are located in a same circumference of diameter 10 mm, which situate at middle of the sample to reduce the influence of different position to the temperature measurement, given the axial symmetry of the heating system. All the thermocouples were inserted from the bottom of samples and upward. The first thermocouple was placed 2 cm above the sample surface, and the second thermocouple was 1 cm above the sample surface, the third thermocouple was inside of sample. The setup used for temperature measurements and detail of thermocouples position are shown in Fig. 2.

3. Results and discussion

3.1. LOI and UL-94 analysis

The UL-94 test results of the EP composites are shown in Table 1,