A simple synthesis of guaiacol based reactive flame retardant and its application in epoxy resins

Yuan Gao[a], Huajun Duan[*a,b], Jin Kang[a], Juan Zhang[a], Yuan Chen[a], Weipeng Liu[a], Ya Li[a]

a *School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, PR China*

b *Institute of Advanced Material Manufacturing Equipment and Technology, Wuhan University of Technology, Wuhan 430070, PR China*

2.1. Materials

1,4-Phthalaldehyde (99.0%), guaiacol (98.0%) and p-Toluenesulfonic acid monohydrate (P-TSA, 98.5%) were obtained from Aladdin Biochemistry Technology Co., Ltd (Shanghai, China). DOPO (99.5%) and anhydrous ethanol (99.0%) were supplied by Wengjiang Chemical Reagent Co., Ltd (Guangdong, China). Epoxy resin (DGEBA, epoxy value: 0.51 mol/100 g) and 4, 4'-diamino-diphenyl methane (DDM, 98.0%) were provided by Baling Huaxing Petrochemical Co., Ltd (Yueyang, China). All the above materials can be used without further purification.

2.4. Characterization

Fourier transform infrared spectra (FT-IR) of the samples were obtained with a Nicolet 6700 infrared spectrometer (Nicolet, USA). The range of the tested wave numbers was 4000-400 cm^{-1} and potassium bromide was used for pressing.

^{1}H, ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AV400 NMR spectrometer (Bruker, Switzerland) with deuterated dimethyl sulfoxide (DMSO-d6) as solvent.

High-resolution mass spectra (HRMS) of PGD were obtained by Q Exactive (Thermo Scientific, USA) .

Differential scanning calorimetry (DSC) thermograms were performed on a Perkin-Elmer DSC 4000 (PerkinElmer, USA) .The heating rates were 5 ℃/min, 10 ℃/min, 15 ℃/min and 20 ℃/min, and all samples were heated from room temperature to 250 ℃.

Thermogravimetric analysis (TGA) was carried out using a STA 449 F3 Jupiter thermal analyser (NETZSCH, Germany). The mass of the test samples was about 5.0 mg and the heating rate was 10 ℃/min. All samples were heated from room temperature to 800 ℃ under N_2 atmosphere.

Dynamic mechanical analysis (DMA) was performed using a Pyris Diamond Dynamic Mechanical Analyser (PerkinElmer, USA). Samples with dimensions of 40×6×3 mm^3 were tested for bending at a temperature range of 40-200 ℃ with a heating rate of 5 ℃/min and a constant frequency of 1 Hz.

LOI values were measured by a JF-3 oxygen index meter (Jiangning, China). According to ASTM D2863-06 standard, the size of the sample strips are 100×6.5×3mm^3. Samples were measured five times and averaged.

Vertical combustion (UL-94) test was carried out on NK8017A instrument (Nklsky, China), according to the GB/T 2408-2008 standard, the size of the sample strip is 130×13×3 mm^3, the sample was measured five times to take the average value.Vertical burning (UL-94) results were obtained from NK8017A instrument (Nklsky, CN).

The fire resistance of epoxy thermosets was further evaluated by the FTT-0007 cone calorimeter (Motis, China) based on the ISO 5660 standard under thermal radiation of 50 kW/m^2. The specimen size was 100×100×3 mm^3 and the data reported are the average of three specimens.

The residual charcoal after cone calorimeter tests was subjected to micromorphological observation using a scanning electron microscope (SEM, JEOL, Japan) model S-4700 at an accelerating voltage of 15 kV.

Raman spectroscopy (Renishaw, UK) was used to measure the graphitisation of the char residues after combustion. The scanning range was 800-2000 cm^{-1} and the laser wavelength was 633 nm.

Universal testing machine (Instron 5967, USA) was employed to assess the tensile and flexural behaviors of EP and EP/PGD samples. The standard of ASTM D638 was used for this tensile test while flexural property was tested according to ASTM D790. Samples of each formula were tested for five times.

3.2. Curing behavior

$$\ln(\beta) = \ln\left(AE_c/R\right) - 1.052E_c/RT_p - 5.311 \quad \text{(S1)}$$

$$\ln\left(\beta/T_p^{\,2}\right) = \ln\left(AR/E_c\right) - E_c/RT_p \quad \text{(S 2)}$$

β is the rate of temperature increase, R is the ideal gas constant 8.314 J/(mol·K), A is the pre-exponential factor, and Tp was is peak exothermic temperature of curing.

3.3. Heat resistance and mechanical properties

$$\nu_e = E'/3RT \quad \text{(S 3)}$$

Among them, T is the thermodynamic temperature at T_g+40 °C, R is the ideal gas constant 8.314 J/(mol·K), and E' is the energy storage modulus at T_g+40 °C.