

# Supporting Information

## A Bio-based Hyperbranched Flame Retardant towards the fire-safety and smoke-suppression Epoxy Composite

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### Characterizations

A nuclear magnetic resonance spectrometer (NMR, Bruker 400M) was used with D<sub>2</sub>O as the solvent to obtain <sup>1</sup>H NMR and <sup>31</sup>P spectra. Scanning Electron Microscope (SEM, Hitachi SU8000) was utilized to examine the microscopic morphologies of FRs and composites. The functional groups and chemical characterization were identified using the FTIR spectrometer (Bruker Vetex-70 IR). Elemental compositions were determined using Energy-dispersive X-ray spectroscopy (EDS, FEI Inspect F50) and Thermo Scientific X-ray photoelectron spectroscopy (XPS). Raman spectra of the char layer were collected using a Raman microspectrometer (HORIBA LabRAM HR 800). A TG Q500 was used to carried out the thermal stability studies with the following conditions: the range of 30 to 800 °C, the heating rate of 10 °C min<sup>-1</sup>, a nitrogen flow of 40 mL min<sup>-1</sup>. Curing behavior was evaluated using a differential scanning calorimetry instrument (DSC, TA Q2000), under a high-purity nitrogen atmosphere and a flowing rate of 50 mL min<sup>-1</sup>. Samples were heated at various rates (5, 10, 15, 20, and 25°C min<sup>-1</sup>) from 30 to 300°C. FTIR were coupled with TG to investigate the decomposed volatile pyrolysis products of composites. Limiting Oxygen Index (LOI) values were measured according to ASTM D2863 using a JF-5 oxygen index apparatus from Nanjing Jiangning Instrument Factory in China. The sample dimensions were 130 mm × 6.5 mm × 3.2 mm. UL-94 ratings were determined according to ASTM D3801 on a CZF-4 instrument from Jiangning in China. The sample dimensions used were 130 mm × 13 mm × 3.2 mm. According to

ISO5660, a cone calorimeter from Fire Testing Technology in UK) was applied to obtain combustion behavior. The dimension of measured samples and exposed heat flux in test was 100 mm×100 mm×3 mm and 35 kW/m<sup>2</sup>, respectively. A pyrolyzer (CDS 5200) and an Agilent 7890B-5977B gas chromatography-mass spectrometer were used with He atmosphere to conduct Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) test. The test parameters included an injector temperature of 40 °C for 3 minutes, followed by an increase to 280 °C at a rate of 10°C/min, and maintenance at 280 °C for 10 minutes. The temperature of interface was 280 °C and the temperature of crack was 500 °C. The Criterion 40 of MTS SANS series in China was adopted to test the mechanical properties of EP and composites. According to per GB/T 1042.2-2006 and GB/T 9341-2000, the tensile and flexural strength were measured respectively. Impact strength was determined at room temperature using a ZBC4000 instrument from the MTS SANS series, following GB/T 1043.1-2008.