

Insight into Hyper-Branching Aluminum Phosphonate in Combination with Multiple Phosphorus Synergies for Fire-Safe Epoxy Resin Composites

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Characterization

¹H and ³¹P nuclear magnetic resonance (¹H and ³¹P NMR) spectra were recorded on an AVANCE 400 Bruker spectrometer at room temperature using DMSO-d and D₂O as the solvent, respectively.

Fourier transform infrared (FTIR) spectra were obtained by a Nicolet 6700 spectrometer (Nicolet Instrument Company, USA) using KBr pellets. The wavenumber range was 400–4000 cm^{−1} and the resolution was 4 cm^{−1}.

The crystal-phase properties of the samples were analyzed with a powder X-ray diffractometer (XRD) (Japan Rigaku D Max-Ra) using a rotating anode X-ray diffractometer equipped with a Ni filtered Cu-Kα tube ($\lambda = 1.54178 \text{ \AA}$) in the 2 θ range from 10° to 70° with a scanning rate of 4 min^{−1}.

The thermal stability was determined by thermogravimetric analysis (TGA), which was performed using a Q5000IR (TA Instruments) thermo-analyzer instrument at a linear heating rate of 20 °C/min from room temperature to 800 °C under nitrogen atmosphere.

Limiting oxygen index (LOI) test was conducted using a HC-2 oxygen index meter (LOI analysis instrument company, Jiangning, China) according to ASTM D2863. Size of the specimens for the measurement was 100 × 6.5 × 3.0 mm³.

Vertical burning UL-94 test was performed on a CFZ-II horizontal and vertical burning tester (Jiangning Analysis Instrument Co., China) with the sample dimension of 127 × 12.7 × 3 mm³ according to ASTM D3801.

The combustion behaviors of the control EP and its composites were tested with a cone calorimeter (Stanton Redcroft, UK) according to ISO 5660 standard. Each specimen with size of 100 × 100 × 3 mm³ was wrapped with an aluminum foil and burned at an external heat flux of 35 kW/m².

Real-time Fourier transform infrared spectroscopy (RT-FTIR) was used to study the thermo-oxidative degradation of samples. The FTIR spectra were recorded in the range of room temperature to 600 °C at a heating rate of 10 °C/min under air on a MAGNA-IR 750 spectrometer (Nicolet Instrument Company, USA).

Thermogravimetric-Fourier transform infrared spectroscopy (TG-FTIR) was conducted with a TGA Q5000 thermogravimetric analyzer, coupled with a Nicolet 6700 spectrophotometer by a stainless steel transfer pipe. Thermal analyzer was conducted in the range from room temperature to 800 °C with a heating rate of 20 °C/min under inert condition.

The morphology of flame retardant and the char layers of the samples after cone test were investigated by using scanning electron microscope (SEM; KYKY1010B, Shanghai Electron Optical Technology Institute, China). The samples were coated with gold/palladium alloy.

Raman spectra of the char residues were obtained using a SPEX-1403 laser Raman spectrometer (SPEX Co., USA) from 500 to 2000 cm^{-1} .

Table S1. Assignments of the peaks in FTIR spectra of cured epoxy resin and its composites.

FTIR (cm^{-1})	Assignments
3412	Stretching vibration of O-H groups
2875–2966	Stretching vibrations of $-\text{CH}_2$ and $-\text{CH}_3$
1090	Stretching vibration of P-O-C
1603	Stretching vibration of C=C
1110	O-H bending vibration
1502	Fingerprint (C-O stretching vibration, $-\text{CH}_3$, $-\text{CH}_2$ - and $-\text{CMe}_2$ -deformation vibration)
1250	Stretching vibration of P=O
1090	Stretching vibration of O=P-O
820,747	C-H bending, rocking vibration

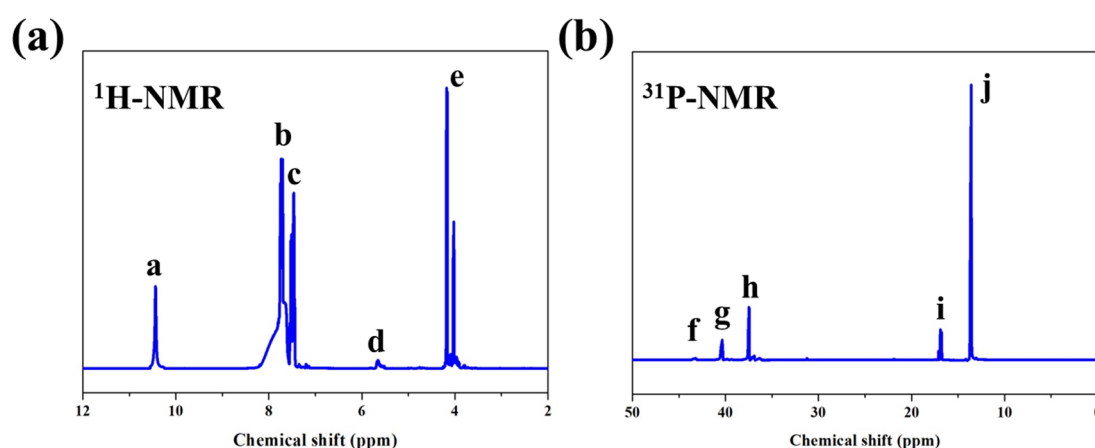


Figure S1. The ^1H NMR spectrum (a) and ^{31}P NMR spectrum (b) of HPP with DMSO- d_6 as the solvent.

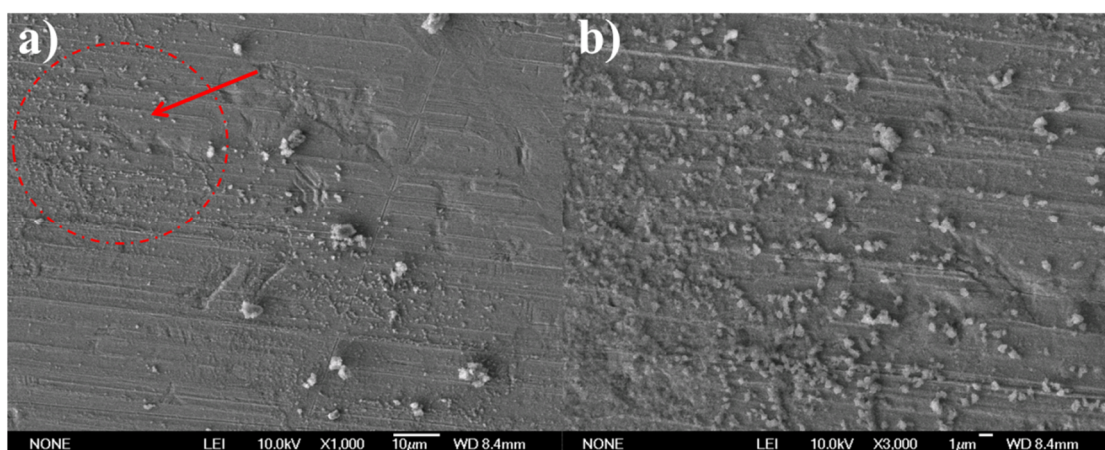


Figure S2. SEM observations of submicro-scaled AHPP: low-magnification (a) and magnified image (b).

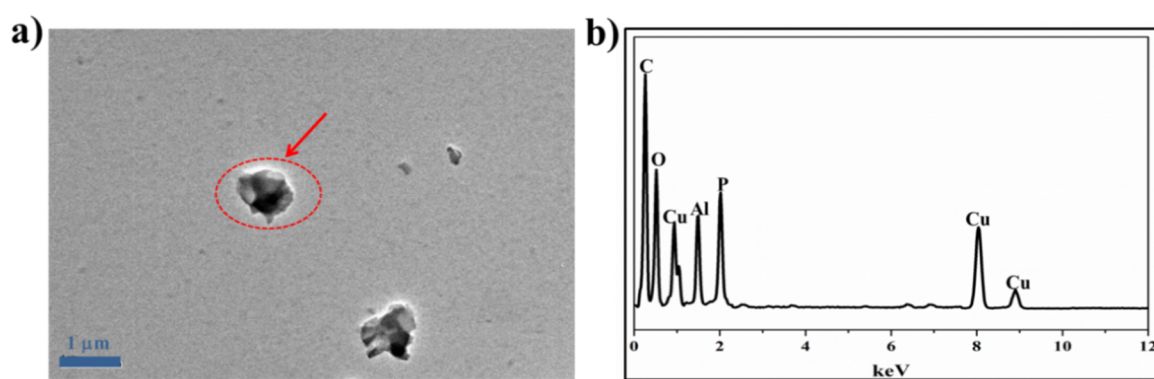


Figure S3. TEM image (a) and EDX spectrum (b) of submicro-scaled AHPP.

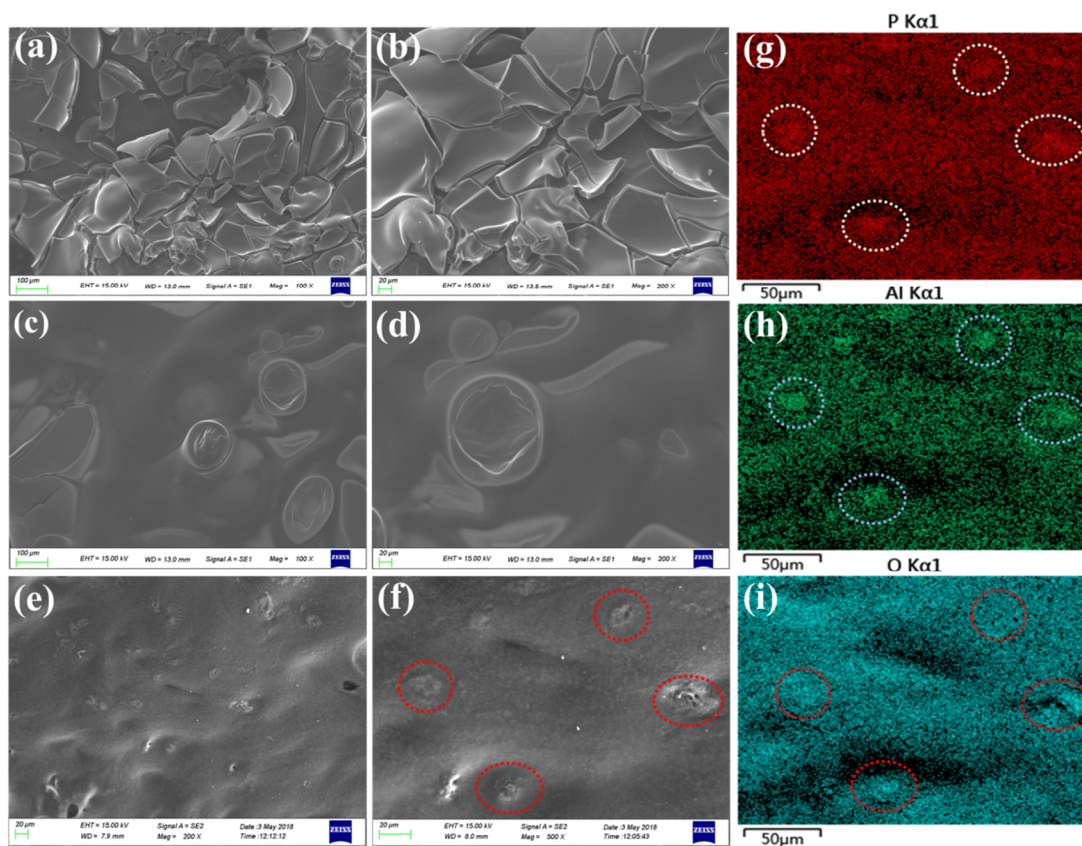


Figure S4. SEM micrographs of the char residue of pristine EP (a,b), EP/DOPO-AHPP (c,d), and EP-AHPP (e,f), and elemental distribution from EDX mapping of the EP-AHPP composite (g–i).