Core-Shell ZIF67@ZIF8 Modified with Phytic Acid as an Effective Flame Retardant for Improving the Fire Safety of Epoxy Resin

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S2.5. Characterization

The X-ray diffraction (XRD) patterns were recorded with D8 DISCOVER A25 using Cu Ka radiation (k = 1.54056 Å) at a scanning speed of 2°/min and a diffraction angle range of 5-70°.

Fourier transform infrared (FTIR) spectra were conducted on a WQF-310 spectrometer with KBr pellets.

Transmission electron microscope (TEM) images were carried out using an FEI Talos F200X microscope at an acceleration voltage of 200 kV.

The morphology and fractured surface were recorded on a FEI Verios G4 scanning electron microscope (SEM). The accelerating voltage was set to 15 kV. The samples were previously coated with a conductive layer of gold.

Thermogravimetric analysis (TGA) was investigated with a linear heating rate of 10 °C min^{-1} from room temperature to 800 °C under nitrogen atmosphere by using a TGAQ50 instrument. And a range of specimen mass from 6 to 10 mg, every sample is measured three times on average.

X-ray photoelectron spectroscopy (XPS) spectra were performed on Axis Supra.

The UL-94 vertical burning test was conducted with a ZR-02 instrument with

dimensions of 130 x 13 x 3 mm^3 according to the ASTM-D-3801.

Limiting oxygen index (LOI) was performed with dimensions of 130 x 6.5 x 3 mm^3 based on a standard ASTM D 2863-77.

Cone calorimetry tests were tested by 6810 with the dimension of the sample sheets of 100 × 100 × 3 mm^3 according to ISO 5660 standard with a heat flux of 35 kW/m^2.

Raman spectra were collected using the Raman micro-spectroscopy system (Alpha300R) with a back-scattering geometry and a wave length of 532 nm. For each sample, three Raman spectra were collected at different positions.

Dynamic mechanical analysis (DMA) test was conducted with a DMA 800 from 40 °C to 250 °C at a rate of 5 °C/min and 1 Hz frequency.

Dispersion of PA-ZIF67@ZIF8 in the EP matrix

Meanwhile, the dispersion of 5 wt% ZIF67@ZIF8 and 5 wt% PA-ZIF67@ZIF8 in epoxy is further characterized by TEM (Figure S1**)**. Obviously, the ZIF67@ZIF8 and PA-ZIF67@ZIF8 are dispersed uniformly without aggregation.

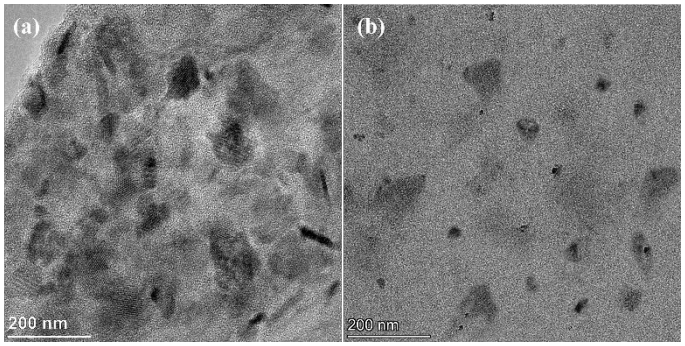

Figure S1 TEM images of (a) ZIF67@ZIF8, and (b) PA-ZIF67@ZIF8.

The mechanical properties of the EP and its composites

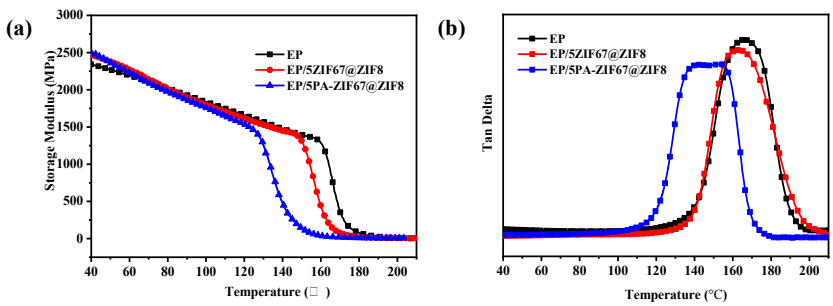

Figure S2 The (a) storage modulus and (b) tan delta of EP and its composites as a function of temperature.

The mechanical properties of the EP and its composites are further studied by DMA. Figure S2 presents the storage modulus and tan delta of EP and EP composites as a function of temperature. With the addition of 5 wt% fillers, the storage modulus of EP composites at 40 ℃ is higher than that of pure EP. In particular, the storage modulus of EP/5PA-ZIF67@ZIF8 is increased from 2340 to 2503 MPa, caused by improved interaction between PA-ZIF67@ZIF8 and EP matrix. Meanwhile, the peak of figure tan delta is regarded as the glass transition temperature (Tg). The glass transition temperature of each sample is decreased compared with pure EP.

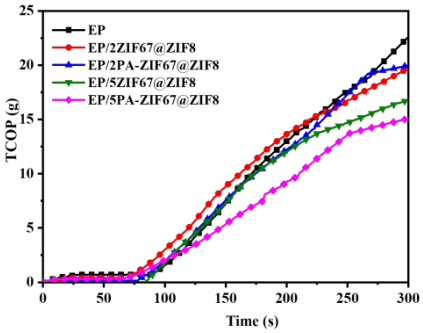

Figure S3 TCOP curves of EP and its nanocomposites

Total CO production (TCOP) curves of the EP and its composites is shown in Figure S3, the TCOP of EP reaches up to 22.6 g, while the EP/5PA-ZIF67@ZIF8 reduces by 37.7% relative to EP.

XRD pattern of the char residue of EP/5PA-ZIF67@ZIF8

The XRD pattern of the char residue of EP/5PA-ZIF67@ZIF8 after cone calorimeter is shown in Figure S4. As shown in Figure S4, the peaks at 2θ=31.6°, 34.6°, 36.2°, 47.3°, 56.4°, 63.1° and 68.0° are corresponded to the characteristic peak of ZnO [1]. In addition, the peaks at 2θ=19.0°, 31.3°, 36.8°, 38.5°, 44.8°, 56.6°, 59.3° and 65.2° are attributable to the characteristic peak of Co_3O_4 [2]. It indicates that the char residue of EP/5PA-ZIF67@ZIF8 contains Co_3O_4 and ZnO after combustion. Both of them would facilitate the generation of residue, achieving better fire safety.

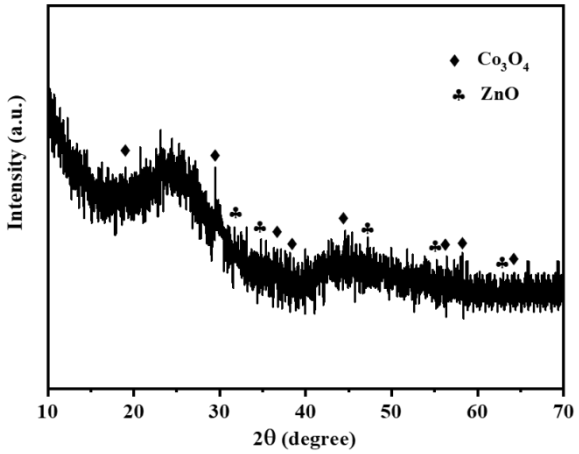

Figure S4 XRD spectrum of char residue of EP/5PA-ZIF67@ZIF8.

References

[1] Ali, T. T.; Basahel, S. N.; Mahmoud, H. A.; Khalil, K. M. S.; Narasimharao, K. Influence of preparation conditions on the catalytic activity of high surface area silica in partial methanol oxidation. Chem. Eng. J. 2017, 330, 852-862.

[2] Xu, W.; Wang, X.; Wu, Y.; Li, W.; Chen, C.Y. Functionalized graphene with Co-ZIF adsorbed borate ions as an effective flame retardant and smoke suppression agent for epoxy resin. J. Hazard. Mater. 2019, 363, 138–151.