

S1. Experimental

S2.1. Materials

Graphite powder (100-120 μm) was provided by Xiamen KnanoTech Port Co. Ltd. Potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$) was supplied by Tianjin Tianli Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) and sulfuric acid (H_2SO_4 , 95~98%) were received from Chengdu Kelong Chemical Co., Ltd. Sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2 , 30% aq.), and acetone were obtained from Guangdong Guanghua Sci-Tech Co., Ltd. 4,4-Diaminodiphenylmethane (DDM), phenylphosphinic acid (PPA), phosphorus pentoxide (P_2O_5), ammonium molybdate ($(\text{NH}_4)_2\text{MoO}_4$), zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and sodium stannate tetrahydrate ($\text{NaSnO}_3 \cdot 3\text{H}_2\text{O}$) were purchased from Aladdin Chemistry Co., Ltd. Epoxy resin (E-51) was bought from Yueyang Petrochemical Co., Ltd.

S2.2 Preparation of MZP-GO

Typically, GO was prepared by an improved Hummers' method [17]. Firstly, 0.10 g of GO was dispersed in 50 mL of CH_3OH with the aid of sonication. 1.34 g of PPA were dispersed in 50 mL of CH_3OH , respectively. The mixture was added into the GO dispersion and the solution was carried out at 80 $^\circ\text{C}$ for 5 h. Then the P-GO was washed several times with CH_3OH and dried at 60 $^\circ\text{C}$ under reduced pressure overnight.

Secondly, 0.10 g of P-GO and 0.40 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were dispersed in 100 mL of water with magnetic stirring for 2 h. 0.38 g of $\text{NaSnO}_3 \cdot 3\text{H}_2\text{O}$ in 50 mL of water was added dropwise at room temperature, followed by 5 h stirring. The precipitate was isolated and washed repeatedly with water. The target product was named as the ZP-GO.

Finally, 0.10 g of ZP-GO was dispersed in 100 mL of deionized water with the aid of sonication at ambient temperature for 30 min, 0.31 g of $(\text{NH}_4)_2\text{MoO}_4$ was added into the mixture which was then allowed to stir for 12 h. When the reaction was over, the product was washed repeatedly with water and the target product was named as the MZP-GO.

S2.3 Preparation of EP and its composites

Fabrication procedure of EP composites with 2.0 wt% MZP-GO were provided as follows: 0.5 g of MZP-GO and 9.9 g of DDM were dispersed in 40 mL of acetone with ultrasonic treatment for 20 min. After that, 36.9 g of EP was poured into the above system with stirring for 3 h. Subsequently, the mixtures were evacuated under a 50 °C vacuum oven for 1 h. After that, the mixtures were cured at 100 °C for 2 h and 150 °C for 2 h. After natural cooling to the normal temperature, the EP/MZP-GO 2.0 composite was successfully prepared. EP composites containing 0.5 wt%, 1.0 wt%, 2 wt% MZP-GO hybrid, which were denoted as EP1, EP2, and EP3, respectively, could be prepared by using the same procedure. For comparison, the pure EP and EP composites containing 2 wt% GO were manufactured by using the same approach (Specific formulations are listed in Table 1).

S2.4. Characterizations

The X-ray diffraction (XRD) patterns were recorded with D8 DISCOVER A25 using Cu K α radiation ($k = 1.54056 \text{ \AA}$) 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 mm³ according to the ASTM-D-3801.

Limiting oxygen index (LOI) was performed with dimensions of 130 x 6.5 x 3 mm³ 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 mm³ according to ISO 5660 standard with a heat flux of 35 kW/m².

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 200 °C at a rate of 5 °C/min and 1 Hz frequency.

Mechanical properties of EP and its composites

The mechanical property of EP and its composites is investigated by DMA. Fig. S1 displays the storage modulus and Tan δ of EP and its composites. It can be seen that the storage modulus of EP composites is increased with the incorporation of MZP-GO content from 0.5 to 2.0 wt%, indicating that MZP-GO served as a fortifier for improving the modulus of EP. In particular, the storage modulus of EP/ MZP-GO 2.0 at 40 °C is increased from 2339 to 2891 MPa, the slightly enhanced storage modulus could presumably be attributed to the high specific surface area and high stiffness of graphene. Meanwhile, the peak of figure Tan δ is regarded as the glass transition temperature (T_g). As shown in Fig. S1b, the T_g values of EP and the EP composites nearly remained invariable, which indicates that no interactions between the modified nanofiller and the epoxy matrix occur in the systems investigated.

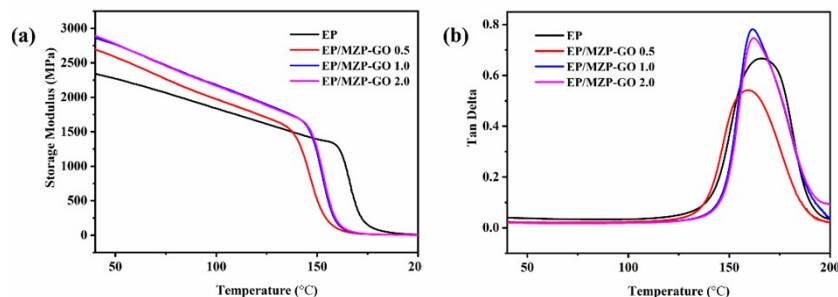


Fig. S1. (a) Storage modulus and (b) Tan δ of the EP and its composites as a function of temperature.