

## Supporting Information

### **Nano-micro Structure of Functionalized Boron Nitride and Aluminum Oxide for Epoxy Composites with Enhanced Thermal Conductivity and Breakdown Strength**

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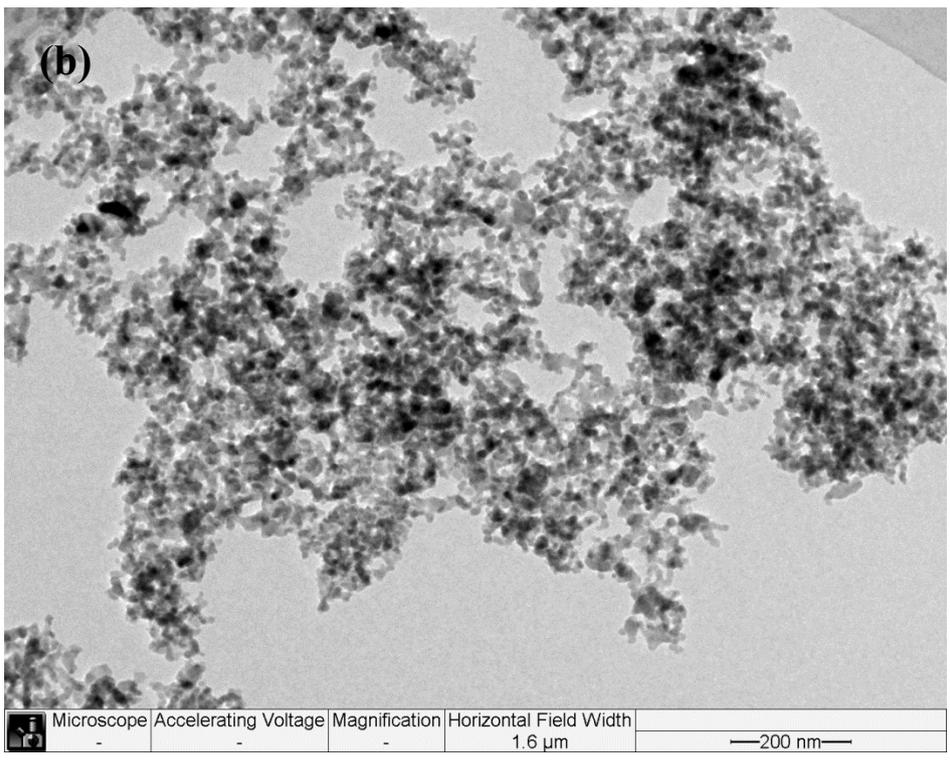
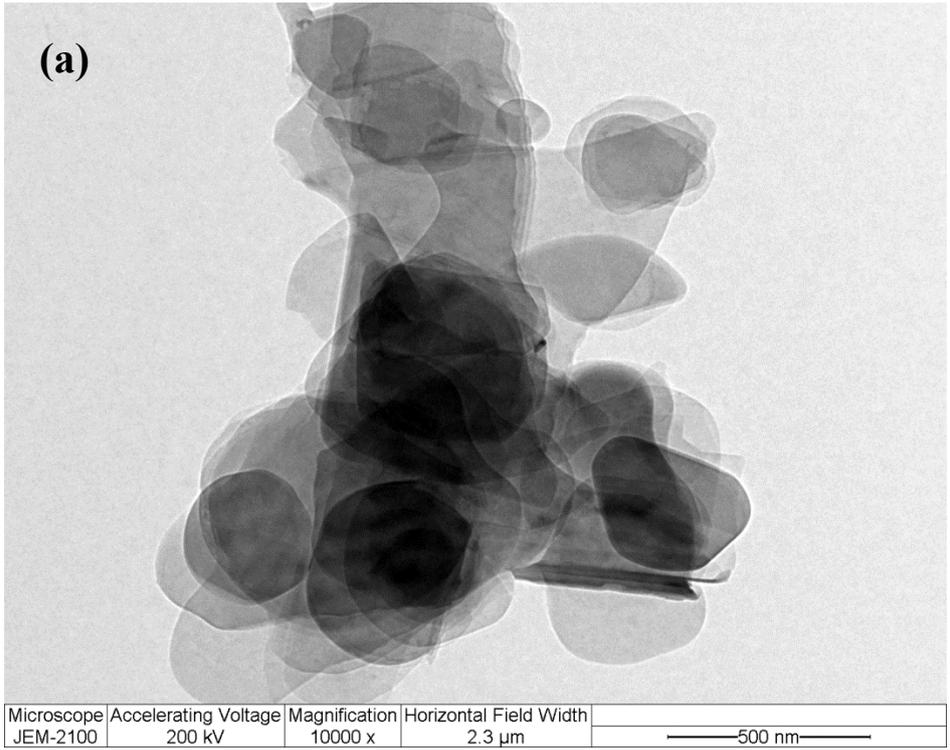


Fig. S1. TEM images of (a) as received BN platelets and (b) as received  $\text{Al}_2\text{O}_3$  particles

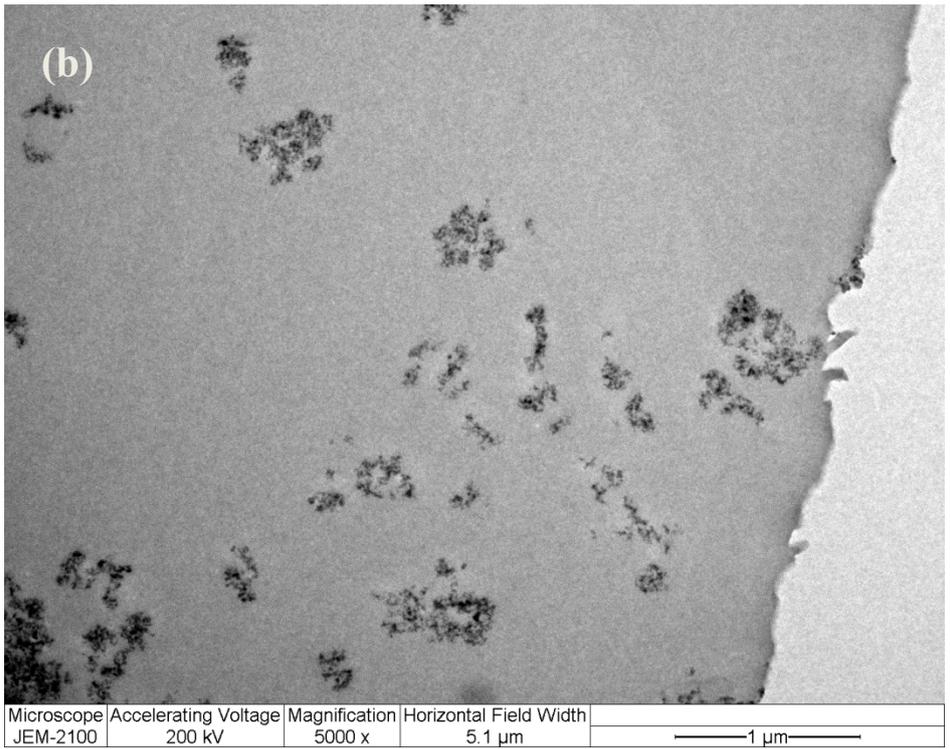
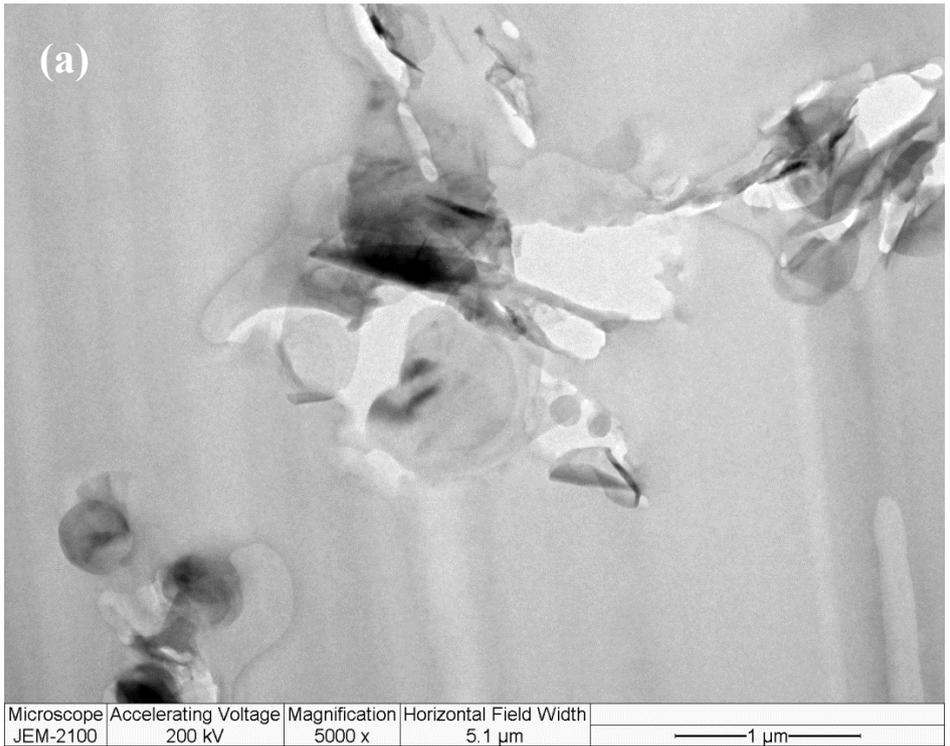


Fig. S2. TEM images of (a) epoxy/BN-HBP and (b) epoxy/ $\text{Al}_2\text{O}_3$ -HBP at 10 wt% filler content

Variation of thermal conductivity as a function of temperature for neat epoxy and its composites with hybrid fillers is studied from 25 to 85 °C. As for neat epoxy, thermal conductivity is 0.186 W m<sup>-1</sup> K<sup>-1</sup> at 25 °C and ascends with increasing temperature. For composites, similar tendency is observed and is consistent with general regulation for highly disordered dielectric materials. Variation of phonon mean free path caused by structure and chain defect scattering could be applied to explain this dependency. The former refers to the propagation of lattice wave in material system and the latter is related to defects introduced during blending which is temperature dependent. Once heated, polymer chains surrounding fillers begin to vibrate and straighten out. As a result, phonon mean free path is increased, implying a higher thermal conductivity. Efficient heat transmission of composites at raised temperatures makes them potential for the next generation thermal interface materials.

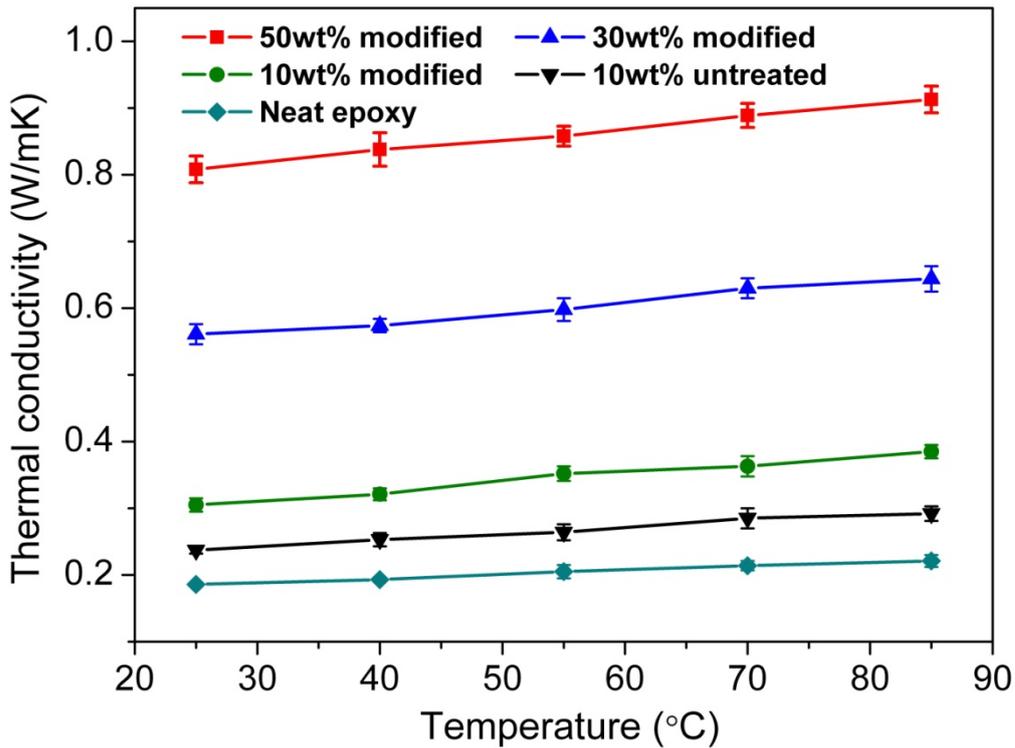
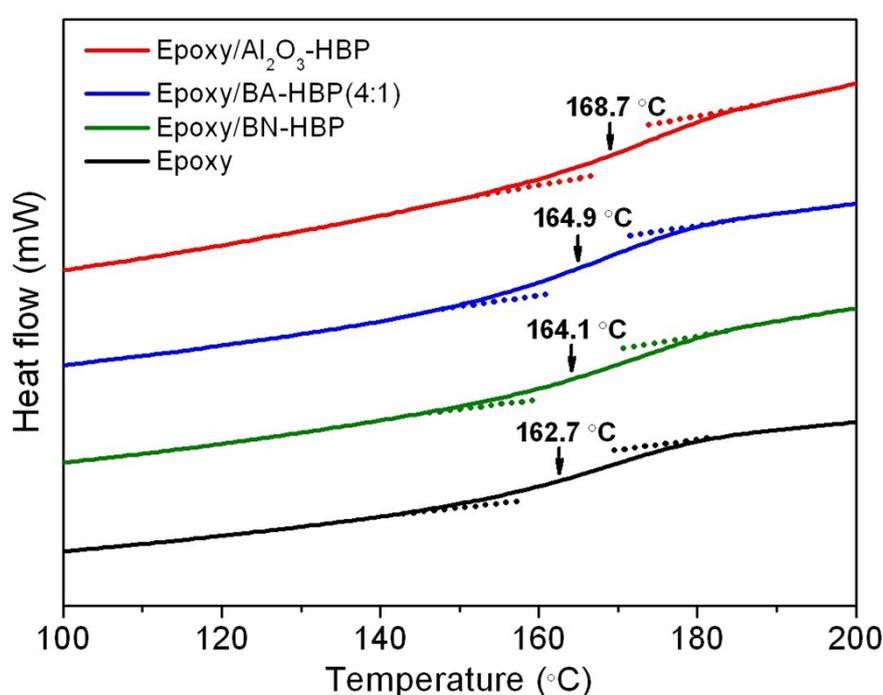


Fig. S3. Thermal conductivity as a function of temperature from 25 to 85 °C for neat epoxy and its composites with hybrid fillers at 4:1 BN-HBP/Al<sub>2</sub>O<sub>3</sub>-HBP (or BN/Al<sub>2</sub>O<sub>3</sub>) weight ratio

Differential Scanning Calorimetry (DSC) is also carried out to measure thermal stability of epoxy composites as shown in **Fig.S4**. Intermediate temperature is denoted as  $T_g$  in this study and neat epoxy presents a value of 162.7 °C. With the addition of modified fillers,  $T_g$ s shift to higher temperatures. For epoxy/ $\text{Al}_2\text{O}_3$ -HBP,  $T_g$  increases by 6.0°C owing to the formation of strong interface through reaction between amino groups of  $\text{Al}_2\text{O}_3$ -HBP and epoxide groups in matrix during curing process.  $T_g$  of epoxy/ $\text{BN}$ -HBP raises by 1.4 °C, not so apparent as epoxy/ $\text{Al}_2\text{O}_3$ -HBP. This can be explained by the relatively weak affinity between basal plane of  $\text{BN}$ -HBP and the matrix. For epoxy/ $\text{BA}$ -HBP(4:1) with hybrid fillers, though  $T_g$  increases by 2.2 °C, no obvious synergistic effect is observed.



**Fig. S4.** DSC curves of neat epoxy and its composites at filler loadings of 10 wt% at a heating rate of 10 °C min<sup>-1</sup> under nitrogen