Supporting Information

Highly thermally conductive polyimide composite films with excellent thermal and electrical insulating properties

*Xuhua He, Yuechuan Wang**

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

*Corresponding author: wangyc@scu.edu.cn

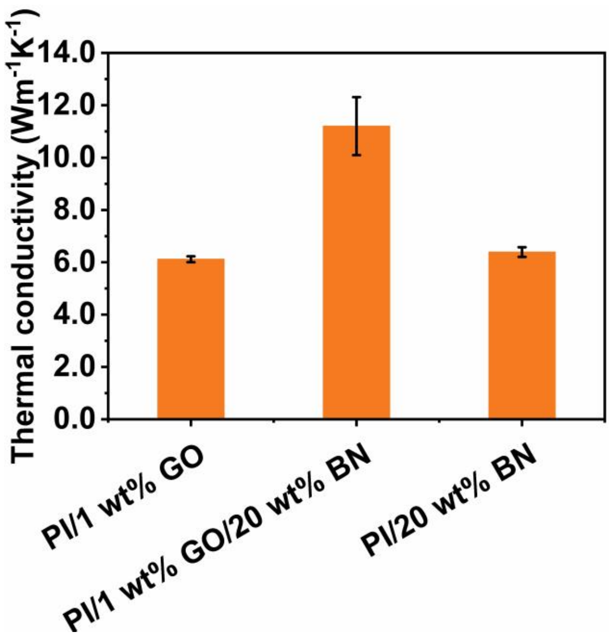

Figure S1. Comparison of the thermal conductivity of PI composites with various fillers.

Theoretical derivations of the thermal conductivity

To theoretically analyze the experimental data, we applied the modified effective medium theory (EMT) model, which works well for multi-phase composites.[1, 2] And the effective thermal conductivity (K^*) of the composites with i kinds of ellipsoidal fillers obeys the following formula

$$\frac{K^*}{K_m} = \frac{\sum_i\left[2\beta_x^i\left(L_x^i - 1\right) + \beta_z^i\left(L_z^i - 1\right)\right] f_i/3 - 1}{\sum_i\left(2\beta_x^i L_x^i + \beta_z^i L_z^i\right) f_i/3 - 1} \quad (1)$$

with

$$\beta_x^i = \frac{K_x^i - K_m}{K_m + L_x^i\left(K_x^i - K_m\right)} \ , \quad (2)$$

$$\beta_z^i = \frac{K_z^i - K_m}{K_m + L_z^i(K_z^i - K_m)} \ , \quad (3)$$

where K_m is the thermal conductivity of the polymer matrix. K_x and K_z represent the thermal conductivities of the ellipsoidal particles along transverse and longitudinal axis, respectively; f is the volume fraction of fillers, and the volume fraction of hybrid fillers with i types satisfies the relationship: $f = \sum_i f_i$, L_x and L_z are the proverbial geometrical depolarization factors dependent on the particle aspect ratio p and given by

$$L_x = \begin{cases} \frac{p^2}{2(p^2-1)} - \frac{p^2}{2(p^2-1)^{3/2}} cosh^{-1}p, & p > 1 \\ \frac{p^2}{2(p^2-1)} + \frac{p^2}{2(p^2-1)^{3/2}} cosh^{-1}p, & p < 1 \end{cases}, \tag{4}$$

$$L_z = 1 - 2L_x.$$

For the special case of the composites with hybrid BN platelets and TGO nanosheets, we can further simplify the formula (1). Usually, p of typical BN and TGO are less than 0.01, resulting in L_x=0, L_z= 1 for both BN and TGO. In addition, because the thermal conductivities of BN and TGO are much higher than that of polymer matrix, we can obtain $\beta_x^1 = K_x^1/K_m, \beta_z^1 = 1$ for BN, and $\beta_x^2 = K_x^2/K_m, \beta_z^2 = 1$ for TGO.

In the hybrid BN/TGO polymer composites, the filler-matrix interfacial thermal resistance (R_k) is of significance. In order to consider such an effect, R_k of BN or TGO can be assumed as a composite unit cell coated with a very thin interfacial thermal barrier layer with thickness d and thermal conductivity K_s. R_k is then defined as $R_k = \lim_{d\to 0,\ K_s\to 0} d/K_s$. Therefore, the effective thermal conductivities of BN and TGO are given by

$$K_1^* = \frac{K_1}{2R_k K_1/l_1 + 1}, K_2^* = \frac{K_2}{2R_k K_2/l_2 + 1}, \tag{5}$$

where K_1^*, K_1, and l_1 represent the effective thermal conductivity, thermal conductivity, and length of the BN, respectively. And K_2^*, K_2, and l_2 represent the effective thermal conductivity, thermal conductivity, and length of the TGO, respectively. The relevant parameters are in **Table S1**.

As a result, the formula (1) for the thermal conductivity enhancement is ultimately simplified as

$$\frac{K^*}{K_m} = \frac{3 + 2f_1(K_1^*/K_m) + 2f_2(K_2^*/K_m)}{3 - (f_1 + f_2)} \tag{6}$$

Table S1. The detailed parameters for calculation.

	BN	TGO	PI matrix
Thermal conductivity ($Wm^{-1}K^{-1}$)	~400[3]	~1500[4]	0.223
Density ($g\ cm^{-3}$)	2.29	~2.20[5]	1.437

Geometry parameters (measured by SEM)	
BN length	20 µm
BN width	10 µm
BN thickness	200 nm
TGO length	80 µm
TGO width	30 µm

References

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